On the lifetimes of evaporating droplets

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The complete description of the lifetime of a droplet on a solid substrate evaporating in a stick-slip mode is obtained. The unexpectedly subtle relationship between the lifetime of such a droplet and those of initially identical droplets evaporating in the extreme modes (namely the constant contact radius and constant contact angle modes) is described. In particular, it is shown that the lifetime of a droplet is not, in general, constrained by those of the extreme modes.

1. Introduction

The evaporation of droplets on solid substrates is not only of fundamental scientific interest but is also of importance in a wide variety of practical applications, such as pesticide spraying, DNA micro-array analysis, inkjet printing, micro-fabrication and spray cooling. In particular, optimising the lifetimes of evaporating droplets may allow considerable efficiencies and economies to be achieved in a variety of industrial contexts. The recent review articles by Cazabat & Guéna (2010) and Erbil (2012) give excellent overviews of the diverse and rapidly expanding literature on droplet evaporation.

The lifetime of an evaporating droplet depends on the manner in which it evaporates. As Picknett & Bexon (1977) described in their pioneering work, there are two "extreme" modes of droplet evaporation, namely the "constant contact radius" (CR) mode in which the contact angle $\theta = \theta(t)$ $(0 \leqslant \theta \leqslant \pi)$ decreases with time t but the contact radius $R = R_0$ remains constant, and the "constant contact angle" (CA) mode in which the contact radius $R = R(t)$ $(\geqslant 0)$ decreases but the contact angle $\theta = \theta_0$ remains constant, where R_0 and θ_0 denote the initial values of R and θ, respectively. However, as Picknett & Bexon (1977) also described (and as Bourgès-Monnier & Shanahan (1995) and many other authors have subsequently confirmed) in practice a droplet usually evaporates in a "stick-slip" (SS) mode made up of one or more "stick" phases in which the contact line is pinned (*i.e.* in which R is constant) and one or more "slip" phases in which the contact line is de-pinned (*i.e.* in which R varies). Various SS modes have been observed experimentally, but perhaps the most commonly reported SS mode is one in which initially there is a stick phase in which the droplet evaporates in a CR phase, followed by a first slip phase in which the droplet evaporates in a CA phase, followed in turn by a second slip phase in which both R and θ vary simultaneously. In practice, the second slip phase is often relatively short, in which case it can be neglected when determining the lifetime of the droplet. Thus, in the present work we study a model for the SS mode sketched in figure 1 (as discussed by, for example, Nguyen & Nguyen (2012b), Stauber *et al.* (2013), and Dash & Garimella (2013)) in which initially the droplet evaporates in a CR phase with $R = R_0$ and with $\theta = \theta(t)$ decreasing from $\theta = \theta_0$ $(0 \leqslant \theta_0 \leqslant \pi)$ to a critical "transition" angle

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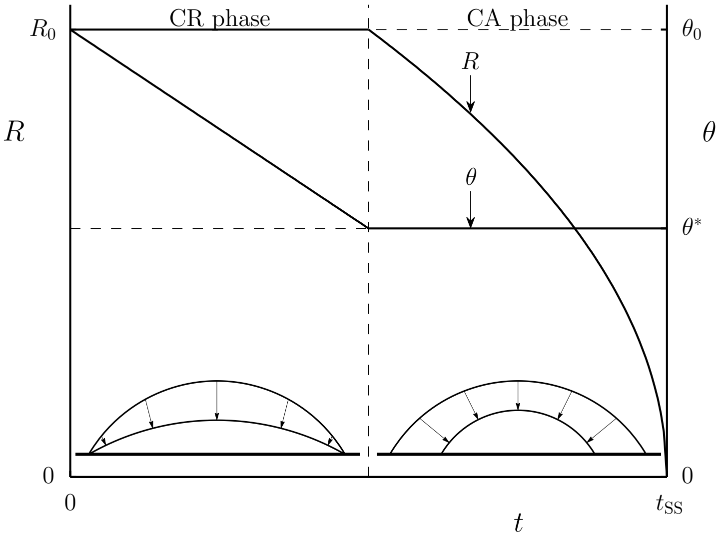

Figure 1. Sketch of the stick-slip (SS) mode considered in the present work in which initially the droplet evaporates in a constant contact radius (CR) phase with $R = R_0$ and with $\theta = \theta(t)$ decreasing from $\theta = \theta_0$ to a critical transition angle $\theta = \theta^*$, after which the droplet evaporates in a constant contact angle (CA) phase with $\theta = \theta^*$ and with $R = R(t)$ decreasing from R_0 to zero.

$\theta = \theta^*$ ($0 \leqslant \theta^* \leqslant \pi$), after which the droplet evaporates in a CA phase with $\theta = \theta^*$ and with $R = R(t)$ decreasing from R_0 to zero. The initial CR phase occurs only if $\theta_0 > \theta^*$; otherwise the contact line is always de-pinned and the droplet simply evaporates in the CA mode. In particular, we verify the model by comparison with the results of relevant physical experiments in the literature and use it to construct a master diagram showing the relationship between the lifetime of a droplet evaporating in this mode and those of initially identical droplets evaporating in the extreme modes for all physically realisable values of the key parameters θ_0 and θ^* which characterise the wettability of the system.

2. The Diffusion-Limited Model

In many situations the evaporation of droplets is well described by the diffusion-limited model, in which diffusion of vapour from the droplet into the surrounding atmosphere is the rate-limiting mechanism (see, for example, Picknett & Bexon (1977), Deegan *et al.* (1997), Hu & Larson (2002), McHale *et al.* (2005), Popov (2005), Dunn *et al.* (2009), Kulinich & Farzaneh (2009), Gelderblom *et al.* (2011), Nguyen & Nguyen (2012a,b), Talbot *et al.* (2012), and Dash & Garimella (2013)).

Assuming that the droplet is sufficiently small that the effect of gravity is negligible, the shape of the droplet will be that of a spherical cap with contact radius $R = R(t)$ ($\geqslant 0$) and contact angle $\theta = \theta(t)$ ($0 \leqslant \theta \leqslant \pi$), and hence volume $V = V(t)$ ($\geqslant 0$) given by

$$V = \frac{\pi R^3}{3} \frac{\sin\theta(2 + \cos\theta)}{(1 + \cos\theta)^2}. \tag{2.1}$$

According to the diffusion-limited model, the rate of change of the droplet volume with respect to time t is

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{\pi R D(c_{\mathrm{sat}} - c_{\infty})}{\rho}\frac{g(\theta)}{(1+\cos\theta)^2}, \tag{2.2}$$

where D is the diffusion coefficient of vapour in the air, ρ is the density of the fluid, c_{sat} is the vapour concentration at the interface, c_{∞} is the vapour concentration far from the interface (which may take values between zero and c_{sat}), and the function $g = g(\theta)$ is given by

$$g(\theta) = (1+\cos\theta)^2\left\{\tan\left(\frac{\theta}{2}\right) + 8\int_0^{\infty}\frac{\cosh^2(\theta\tau)}{\sinh(2\pi\tau)}\tanh\left[\tau(\pi-\theta)\right]\mathrm{d}\tau\right\}. \tag{2.3}$$

Note that $g(0) = 16/\pi$, $g(\pi/2) = 2$, and $g \sim (\pi-\theta)^3\log 2 \to 0^+$ as $\theta \to \pi^-$.

3. Theoretical Predictions for the Lifetimes of Droplets

The lifetime of an evaporating droplet is the time it takes for its volume V to reach zero. Depending on the manner in which it evaporates, this may occur when either its radius R and/or its contact angle θ reach zero, and so the lifetime of a droplet is obtained by integrating (2.2) with respect to t until either $R = 0$ and/or $\theta = 0$, as appropriate. Hence, scaling t with an appropriate reference timescale,

$$\frac{\rho}{2D(c_{\mathrm{sat}} - c_{\infty})}\left(\frac{3V_0}{2\pi}\right)^{2/3}, \tag{3.1}$$

where V_0 is the initial value of V, the lifetime of a droplet evaporating in the CR mode, denoted by $t_{\mathrm{CR}} = t_{\mathrm{CR}}(\theta_0)$, is given by

$$t_{\mathrm{CR}} = \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3}\int_0^{\theta_0}\frac{2\,\mathrm{d}\theta}{g(\theta)}, \tag{3.2}$$

and the lifetime of a droplet evaporating in the CA mode, denoted by $t_{\mathrm{CA}} = t_{\mathrm{CA}}(\theta_0)$, is given by

$$t_{\mathrm{CA}} = \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3}\frac{\sin\theta_0(2+\cos\theta_0)}{g(\theta_0)}. \tag{3.3}$$

The lifetime of a droplet evaporating in the SS mode is denoted by $t_{\mathrm{SS}} = t_{\mathrm{SS}}(\theta_0, \theta^*)$, and is, in general, a function of the transition angle θ^* as well as of the initial contact angle θ_0, and will not, in general, be equal to either t_{CR} or t_{CA} when $\theta_0 > \theta^*$. Specifically, for $0 \leqslant \theta_0 \leqslant \theta^*$ we have $t_{\mathrm{SS}} = t_{\mathrm{CA}}$, where t_{CA} is given by (3.3), but for $\theta_0 \geqslant \theta^*$ we have

$$t_{\mathrm{SS}} = \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3}\left[\int_{\theta^*}^{\theta_0}\frac{2\,\mathrm{d}\theta}{g(\theta)} + \frac{\sin\theta^*(2+\cos\theta^*)}{g(\theta^*)}\right], \tag{3.4}$$

where the first term on the right-hand side of (3.4) represents the duration of the CR phase and the second term represents the duration of the CA phase.

4. Experimental Validation of the Model

Before analysing the theoretically predicted lifetime of an evaporating droplet, t_{SS}, given by (3.4), the model is verified by comparison with the results of relevant physical experiments in the literature for which all of the necessary data are available. In particular, we use the 29 sets of experimental results for droplets evaporating in a SS mode

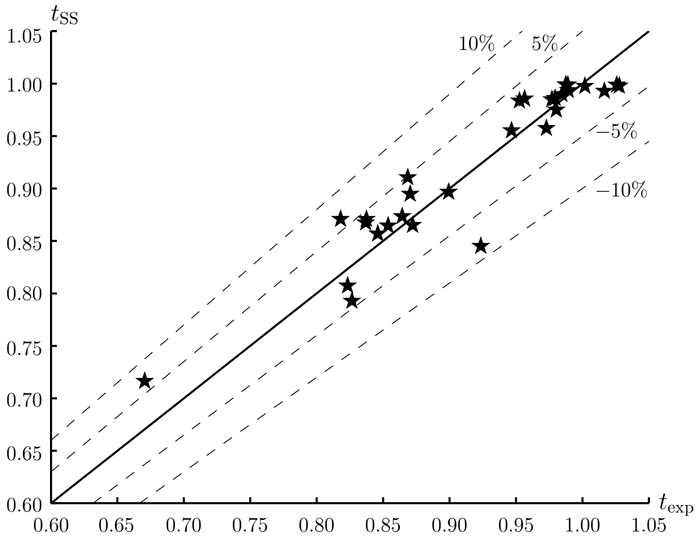

FIGURE 2. The theoretically predicted lifetimes of evaporating droplets, t_{SS}, calculated from (3.4) using the experimentally determined values of θ_0 and θ^* plotted as a function of the corresponding experimentally determined values, t_{exp}, together with a solid line showing $t_{SS} = t_{exp}$ and dashed lines showing 5% and 10% deviations from $t_{SS} = t_{exp}$.

obtained by Bourgès-Monnier & Shanahan (1995), Uno *et al.* (1998), Fukai *et al.* (2006), Li *et al.* (2009), Song *et al.* (2011), Nguyen *et al.* (2012), Lim *et al.* (2012), Yu *et al.* (2012), and Dash & Garimella (2013) for which the duration of the second slip phase was at most 10% of the lifetime of the droplet. For each of these sets of experimental results the experimentally determined lifetime of the droplet, denoted by t_{exp}, was obtained by fitting the experimental data for $V^{2/3}$ as a linear function of t and extrapolating to $V = 0$ (as proposed by, for example, Nguyen *et al.* (2012)). Figure 2 shows t_{SS} calculated from (3.4) using the experimentally determined values of θ_0 and θ^* plotted as a function of the corresponding values of t_{exp} together with a solid line showing $t_{SS} = t_{exp}$ and dashed lines showing 5% and 10% deviations from $t_{SS} = t_{exp}$. In particular, figure 2 shows that the theoretically predicted values are in excellent agreement with the experimentally determined values, with all of the values of t_{SS} lying within 10% of t_{exp} and 26 of the 29 values lying within 5%. Details of the sets of experimental results used in figure 2 (and also subsequently in figure 5) are given in table 1.

5. Results

5.1. *The Lifetimes of Evaporating Droplets*

Figures 3 and 4 show t_{SS}, t_{CR} and t_{CA} plotted as functions of θ_0 for $0 < \theta^* \leqslant \pi/2$ and $\pi/2 \leqslant \theta^* < \pi$, respectively, and show that $t_{CR} < t_{CA}$ when $0 < \theta_0 < \theta_{crit}$, where $\theta_0 = \theta_{crit} \simeq 2.5830$ (*i.e.* $\theta_{crit} \simeq 148^\circ$), but that $t_{CR} > t_{CA}$ when $\theta_{crit} < \theta_0 < \pi$, with $t_{CR} = t_{CA} = t_{SS} = 0$ at $\theta_0 = 0$, $t_{CR} = t_{CA} \simeq 0.9354$ at $\theta_0 = \theta_{crit}$, and $t_{CR} = t_{CA} = t_{SS} = (4^{1/3}\log 2)^{-1} \simeq 0.9088$ at $\theta_0 = \pi$. In particular, figures 3 and 4 illustrate the sometimes overlooked result first obtained qualitatively by Picknett & Bexon (1977) that a droplet evaporating in the CR mode has a shorter lifetime than an initially identical droplet evaporating in the CA mode when $0 < \theta_0 < \theta_{crit}$, but that the opposite is true when

Reference	Figure	Fluid	Substrate
Bourgès-Monnier & Shanahan (1995)	Fig. 1 (stages II–IV) Fig. 2 (stages II–IV)	Water Water	Polished epoxy resin Polished epoxy resin
Uno *et al.* (1998)	Fig. 3(d)	Latex dispersion	ODTES_{100} on glass
Fukai *et al.* (2006)	Fig. 3 Fig. 4 Fig. 5	Water Water Xylene-polystyrene	$\mathrm{SO_3H}$ on silicon $\mathrm{SO_3H}$ on silicon $\mathrm{R_f}$ on silicon
Li *et al.* (2009)	Fig. 5 (all 9 sets)	Water	Dialkyl disulfides on gold-covered mica
Song *et al.* (2011)	Fig. 2	Water	Platinum
Nguyen *et al.* (2012)	Fig. 5 (all 4 sets) Fig. 9(a) Fig. 9(b) Fig. 9(c)	Water Water Water Water	Oct-silicon Oct-silicon OTS-silicon Teflon
Lim *et al.* (2012)	Fig. 4(c) Fig. 6(b)	Water Diethylene glycol with coffee particles	Pyrex glass Pyrex glass
Yu *et al.* (2012)	Figs 2 and 4 (2 μl droplet)	Water	Teflon on PDMS on glass
Dash & Garimella (2013)	Fig. 3 and Table 3 (all 3 sets)	Water	Teflon on silicon

Table 1. Details of the 29 sets of experimental results used in figures 2 and 5. In the "Substrate" column, "ODTES_{100}" denotes octadecyltriethoxysilane with a static contact angle of roughly 100° for pure water, "$\mathrm{SO_3H}$" denotes 3-mercaptopropyltrimethoxysilane, "$\mathrm{R_f}$" denotes perfluorohexylethyltrimethoxysilane, "Oct-silicon" denotes silicon hydrophobised with octanol, "OTS-silicon" denotes silicon hydrophobised with n-octadecyltrichlorosilane in heptane, and "PDMS" denotes polydimethylsiloxane.

$\theta_{\mathrm{crit}} < \theta_0 < \pi$, and that in the special case $\theta_0 = \pi$ the CR, CA and SS modes all coincide (*i.e.* $R \equiv R_0 = 0$ and $\theta \equiv \theta_0 = \pi$ for all t).

Since the SS mode is a simple combination of the extreme modes it would be natural to assume, as some previous authors have done, that the lifetime of a droplet evaporating in this mode is always constrained by the lifetimes of initially identical droplets evaporating in the extreme modes. However, while figures 3 and 4 show that when $0 < \theta_0 \leqslant \pi/2$ (and, in particular, in the thin-film limit $\theta_0 \to 0^+$) it is indeed correct that t_{SS} lies between t_{CR} and t_{CA}, they also show that when $\pi/2 < \theta_0 < \pi$ this result is not, in general, correct. Specifically, figures 3 and 4 show that when $0 < \theta^* < \theta_{\mathrm{crit}}$ (but not when $\theta_{\mathrm{crit}} < \theta^* < \pi$) then $t_{\mathrm{SS}} > \max(t_{\mathrm{CR}}, t_{\mathrm{CA}})$ when θ_0 lies in the interval $\hat{\theta}_0 < \theta_0 < \pi$, where $\hat{\theta}_0 = \hat{\theta}_0(\theta^*)$ is the unique value of θ_0 in the interval $\pi/2 < \theta_0 < \theta_{\mathrm{crit}}$ at which $t_{\mathrm{SS}} = t_{\mathrm{CA}}$. (Note that when $\pi/2 < \theta^* < \theta_{\mathrm{crit}}$ then $\hat{\theta}_0 = \theta^*$.) In other words, when $0 < \theta^* < \theta_{\mathrm{crit}}$ the

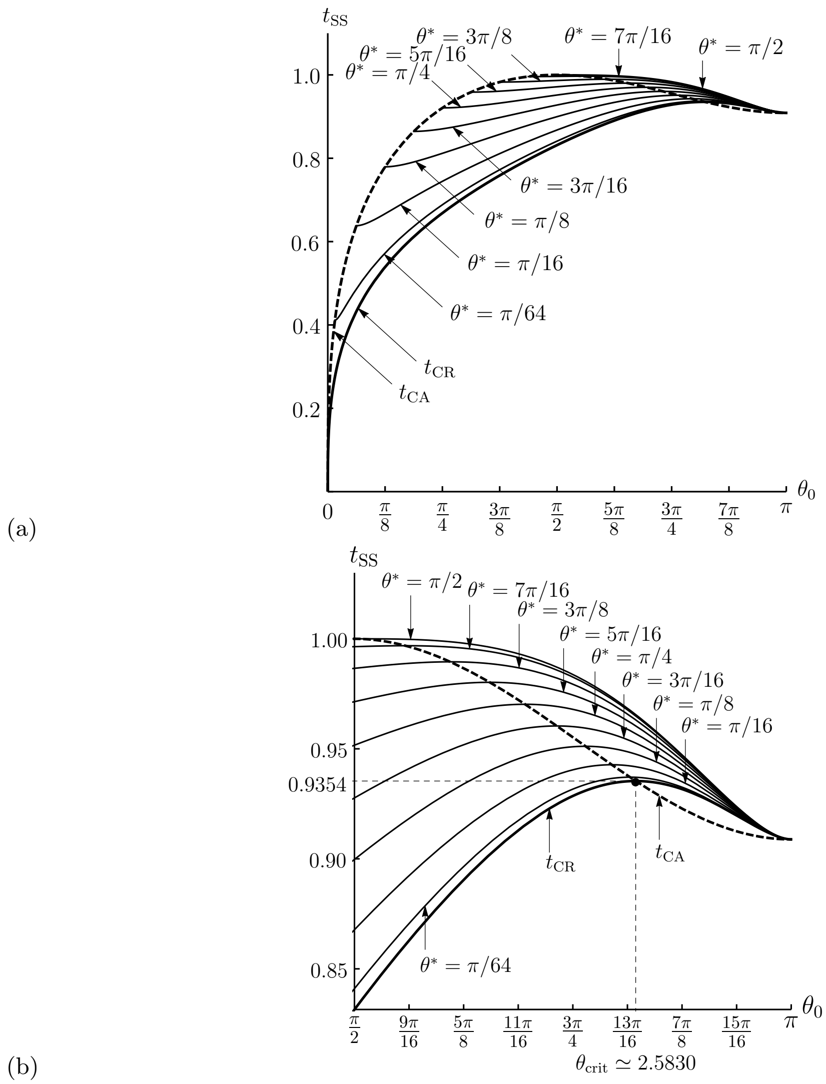

FIGURE 3. Lifetime of an evaporating droplet, $t_{\rm SS}$, given by (3.4) plotted as a function of the initial contact angle θ_0 in the range $0 \leqslant \theta_0 \leqslant \pi$ for transition angles $\theta^* = \pi/64$, $\pi/16$, $\pi/8$, $3\pi/16$, $\pi/4$, $5\pi/16$, $3\pi/8$, $7\pi/16$, $\pi/2$, together with the lifetimes of initially identical droplets evaporating in the CR and CA modes, $t_{\rm CR}$ and $t_{\rm CA}$, given by (3.2) and (3.3), respectively. For clarity, the behaviour in the range $\pi/2 \leqslant \theta_0 \leqslant \pi$ is shown in greater detail in part (b).

lifetime of a droplet evaporating in the SS mode is longer than those of initially identical droplets evaporating in the extreme modes for sufficiently large values of θ_0. Furthermore, for any value of θ^*, figures 3 and 4 show that $t_{\rm SS}(\theta_0, \theta^*) \leqslant t_{\rm SS}(\hat{\theta}_0, \theta^*)$, *i.e.* the longest lifetime of any droplet evaporating in the SS mode always occurs when $\theta_0 = \hat{\theta}_0$, and that $t_{\rm CR}, t_{\rm CA}, t_{\rm SS} \leqslant 1 = t_{\rm CA}(\pi/2)$, *i.e.* the longest lifetime of any droplet evaporating in any of the three modes for all possible values of θ_0 and θ^* is that of a droplet with initial contact angle $\theta_0 = \pi/2$ evaporating in the CA mode. Details of the behaviour of $t_{\rm CR}$, $t_{\rm CA}$ and $t_{\rm SS}$ in appropriate asymptotic limits are given in the next subsection.

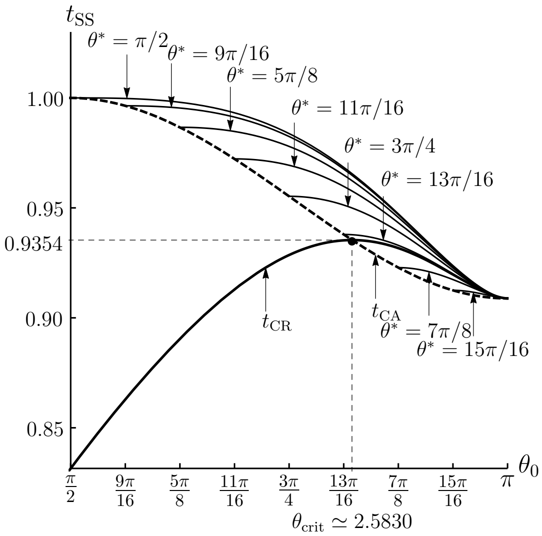

FIGURE 4. As figure 3, except in the range $\pi/2 \leqslant \theta_0 \leqslant \pi$ for transition angles $\theta^* = \pi/2$, $9\pi/16$, $5\pi/8$, $11\pi/16$, $3\pi/4$, $13\pi/16\,(< \theta_{\mathrm{crit}} \simeq 2.5830)$, $7\pi/8\,(> \theta_{\mathrm{crit}})$, $15\pi/16$. For clarity, only the behaviour in the range $\pi/2 \leqslant \theta_0 \leqslant \pi$ is shown.

5.2. *Asymptotic Behaviour of* t_{CR}, t_{CA} *and* t_{SS}

As figure 3 shows, in the limit of small initial contact angle, $\theta_0 \to 0^+$, the curves corresponding to t_{CR} and t_{CA} approach zero from above with infinite slope according to

$$t_{\mathrm{CR}} = \left(\frac{1}{3}\right)^{2/3} \frac{\pi}{2}\,\theta_0^{1/3} + O\left(\theta_0^{4/3}\right) \tag{5.1}$$

and

$$t_{\mathrm{CA}} = \left(\frac{1}{3}\right)^{2/3} \frac{3\pi}{4}\,\theta_0^{1/3} + O\left(\theta_0^{4/3}\right) \tag{5.2}$$

(and hence $t_{\mathrm{CA}} = 3t_{\mathrm{CR}}/2$ at leading order in this limit), $t_{\mathrm{CA}} = 1$ at $\theta_0 = \pi/2$, $t_{\mathrm{CR}} = t_{\mathrm{CA}} \simeq 0.9354$ at $\theta_0 = \theta_{\mathrm{crit}} \simeq 2.5830$, and in the limit of large initial contact angle, $\theta_0 \to \pi^-$, the curves corresponding to t_{CR} and t_{CA} approach the value $(4^{1/3}\log 2)^{-1} \simeq 0.9088$ from above with zero slope according to

$$t_{\mathrm{CR}} = \frac{1}{4^{1/3}\log 2}\left[1 - \frac{4\log 2 - 1}{12\log 2}(\pi-\theta_0)^2\log(\pi-\theta_0)\right] + O\left(\pi-\theta_0\right)^2 \tag{5.3}$$

and

$$t_{\mathrm{CA}} = \frac{1}{4^{1/3}\log 2}\left[1 + \frac{4\log 2 - 1}{24\log 2}(\pi-\theta_0)^2\right] + O\left(\pi-\theta_0\right)^4. \tag{5.4}$$

As figures 3 and 4 show, for all values of θ^* the curve corresponding to t_{SS} departs from the curve corresponding to t_{CA} at $\theta_0 = \theta^*$ with zero slope according to

$$t_{\mathrm{SS}} = t_{\mathrm{CA}}(\theta^*) + A(\theta^*)(\theta_0-\theta^*)^2 + O\left(\theta_0-\theta^*\right)^3, \tag{5.5}$$

in the limit $\theta_0 \to \theta^{*+}$, where the coefficient $A = A(\theta^*)$ is given by

$$A(\theta^*) = \left(\frac{2(1+\cos\theta^*)^2}{\sin\theta^*(2+\cos\theta^*)}\right)^{2/3} \frac{(2\cos^2\theta^* + 2\cos\theta^* - 3)g(\theta^*) - \sin\theta^*(2+\cos\theta^*)g'(\theta^*)}{\sin\theta^*(2+\cos\theta^*)g(\theta^*)^2}, \tag{5.6}$$

where a dash (′) denotes differentiation with respect to argument. In particular, since $A > 0$ for $0 < \theta^* < \pi/2$ but $A < 0$ for $\pi/2 < \theta^* < \pi$, the curve corresponding to t_{SS} has a local minimum at $\theta_0 = \theta^*$ for $0 < \theta^* < \pi/2$ as shown in figure 3(a), but a local maximum at $\theta_0 = \theta^*$ for $\pi/2 < \theta^* < \pi$ as shown in figure 4. Furthermore, in the limit of large initial contact angle, $\theta_0 \to \pi^-$, the curve corresponding to t_{SS}, like the curves corresponding to t_{CR} and t_{CA} described above, approaches the value $(4^{1/3}\log 2)^{-1} \simeq 0.9088$ with zero slope according to (5.3) to the order of accuracy shown.

As figure 3(a) shows, in the limit of small transition angle, $\theta^* \to 0^+$, the curve corresponding to t_{SS} approaches the curve corresponding to t_{CR} from above for all values of θ_0 according to

$$t_{\mathrm{SS}} = t_{\mathrm{CR}}(\theta_0) + \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3} \frac{\pi}{16}\theta^* + O\left(\theta^{*2}\right). \tag{5.7}$$

As figure 4 shows, in the limit of large transition angle, $\theta^* \to \pi^-$, the curve corresponding to t_{SS} approaches the curve corresponding to t_{CA} from above for all values of θ_0 in the vanishingly small range $\theta^* < \theta_0 < \pi$ according to

$$t_{\mathrm{SS}} = \frac{1}{4^{1/3}\log 2}\left[1 + \frac{4\log 2 - 1}{24\log 2}(\pi-\theta_0)^2\left\{1 - 2\log\left(\frac{\pi-\theta_0}{\pi-\theta^*}\right)\right\}\right] + O\left(\pi-\theta_0\right)^4. \tag{5.8}$$

5.3. *Master Diagram*

The relationship between the lifetimes of initially identical droplets evaporating in the three different modes is summarised in the master diagram presented in figure 5, which shows how the θ_0–θ^* parameter plane is divided up into regions in which the six possible orderings of t_{CR}, t_{CA} and t_{SS} occur. Specifically, region I corresponds to $t_{\mathrm{CR}} < t_{\mathrm{SS}} < t_{\mathrm{CA}}$, region II to $t_{\mathrm{CR}} < t_{\mathrm{CA}} < t_{\mathrm{SS}}$, region III to $t_{\mathrm{CA}} < t_{\mathrm{CR}} < t_{\mathrm{SS}}$, region IV to $t_{\mathrm{CA}} < t_{\mathrm{SS}} < t_{\mathrm{CR}}$, region V to $t_{\mathrm{SS}} = t_{\mathrm{CA}} < t_{\mathrm{CR}}$, and region VI to $t_{\mathrm{CR}} < t_{\mathrm{SS}} = t_{\mathrm{CA}}$. In particular, figure 5 shows that these are the only possible orderings that can occur. For example, there are no parameter values for which $t_{\mathrm{SS}} < \min(t_{\mathrm{CR}}, t_{\mathrm{CA}})$, *i.e.* the lifetime of a droplet evaporating in the SS mode can never be less than both of the lifetimes of initially identical droplets evaporating in the extreme modes. The upper left-hand half of the parameter plane (*i.e.* regions V and VI), $\theta_0 > \theta^*$, corresponds to situations in which the SS and CA modes coincide, and so, in particular, the behaviour is independent of θ^*. More interesting behaviour occurs in the lower right-hand half of the parameter plane (*i.e.* regions I–IV), $\theta_0 < \theta^*$, in which the SS mode has both a CR and a CA phase. In particular, approximately 53% of it is occupied by regions II and III in which $t_{\mathrm{SS}} > \max(t_{\mathrm{CR}}, t_{\mathrm{CA}})$, *i.e.* in which the lifetime of a droplet evaporating in the SS mode is longer than the lifetimes of initially identical droplets evaporating in the extreme modes.

Figure 5 also includes points corresponding to the 29 sets of experimental results shown previously in figure 2. Note that since all of these sets of experimental results include the initial CR phase they all have $\theta_0 > \theta^*$, and hence all of the points lie in the lower right-hand half of the parameter plane. In particular, for each set of experimental results the appropriate point in the θ_0–θ^* parameter plane is denoted by a solid circle if the experimentally determined lifetime of the droplet, t_{exp}, is correctly ordered with respect to the theoretically predicted values of t_{CR} and t_{CA}, and by an open circle if it

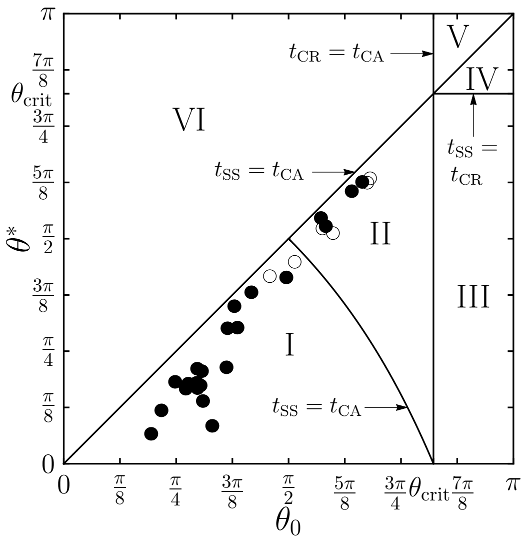

FIGURE 5. Master diagram showing how the θ_0–θ^* parameter plane is divided up into regions in which the six possible orderings of the lifetimes of initially identical droplets evaporating in the CR, CA and SS modes occur. Region I corresponds to $t_{\mathrm{CR}} < t_{\mathrm{SS}} < t_{\mathrm{CA}}$, region II to $t_{\mathrm{CR}} < t_{\mathrm{CA}} < t_{\mathrm{SS}}$, region III to $t_{\mathrm{CA}} < t_{\mathrm{CR}} < t_{\mathrm{SS}}$, region IV to $t_{\mathrm{CA}} < t_{\mathrm{SS}} < t_{\mathrm{CR}}$, region V to $t_{\mathrm{SS}} = t_{\mathrm{CA}} < t_{\mathrm{CR}}$, and region VI to $t_{\mathrm{CR}} < t_{\mathrm{SS}} = t_{\mathrm{CA}}$. In particular, note that $t_{\mathrm{SS}} > \max(t_{\mathrm{CR}}, t_{\mathrm{CA}})$ in regions II and III. For each set of experimental results the appropriate point is denoted by a solid circle if the experimentally determined lifetime of the droplet, t_{exp}, is correctly ordered with respect to the theoretically predicted values of t_{CR} and t_{CA}, and by an open circle if it is not.

is not. As figure 5 shows, all of the points are in regions I and II, and 23 of the 29 sets of experimental results are correctly ordered, providing encouraging support for the present theoretical predictions. However, note that since all of the sets of experimental results shown correspond to values of θ_0 satisfying $\theta_0 < \theta_{\mathrm{crit}}$, there are no points in regions III and IV, and so testing the present theoretical predictions for superhydrophobic droplets with $\theta_0 > \theta_{\mathrm{crit}}$ remains an open challenge.

6. Conclusions

In the present work we obtained the complete description of the unexpectedly subtle relationship between the lifetime of a droplet on a solid substrate evaporating in a SS mode and those of initially identical droplets evaporating in the extreme modes. In particular, the master diagram presented in figure 5 shows that the lifetime of a droplet is not, in general, constrained by those of the extreme modes.

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