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Comment on "Increased evaporation kinetics of sessile droplets by using nanoparticles" by Nguyen and Nguyen

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In a recent paper Nguyen and Nguyen [1] proposed a simple but very useful model for what they termed the "combined pinned-receding mode" of evaporation of a fluid droplet on a solid substrate. Their model is based on the widely-used "diffusion-limited" model, in which diffusion of vapour from the droplet into the surrounding atmosphere is the rate-limiting mechanism (see, for example, Picknett and Bexon [2] and Popov [3]). According to the diffusion-limited model, for a small droplet whose shape is that of a spherical cap with contact radius $R = R(t)\,(\geq 0)$ and contact angle $\theta = \theta(t)\,(0 \leq \theta \leq \pi)$, and hence volume $V = V(t)\,(\geq 0)$ given by

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

the rate of change of V with respect to time t is given by

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

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, and the function $g = g(\theta)$ is given by

$$g(\theta) = (1+\cos\theta)^2 \left\{ \tan\left(\frac{\theta}{2}\right) + 8\int_0^\infty \frac{\cosh^2(\theta\tau)}{\sinh(2\pi\tau)} \tanh\left[\tau(\pi-\theta)\right] \mathrm{d}\tau \right\}. \tag{3}$$

Note that $g(0) = 16/\pi$, $g(\pi/2) = 2$, and $g(\pi) = 0$. The initial values of θ, R and V at $t = 0$ are denoted by θ_0, R_0 and V_0, respectively.

As Picknett and Bexon [2] described in their pioneering work, there are two "pure" modes of droplet evaporation, namely the "constant radius" (CR) mode in which the contact angle θ decreases but the contact radius $R = R_0$ remains fixed, and the "constant angle" (CA) mode in which the contact radius R decreases but the contact angle $\theta = \theta_0$ remains fixed. According to the diffusion-limited model the scaled lifetimes of a droplet evaporating in the CR mode, denoted by $t_{\mathrm{CR}} = t_{\mathrm{CR}}(\theta_0)$, and of a droplet evaporating in the CA mode, denoted by $t_{\mathrm{CA}} = t_{\mathrm{CA}}(\theta_0)$, are given by

$$t_{\mathrm{CR}} = \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3} \int_0^{\theta_0} \frac{2\,\mathrm{d}\theta}{g(\theta)} \tag{4}$$

and

$$t_{\mathrm{CA}} = \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3} \frac{\sin\theta_0(2+\cos\theta_0)}{g(\theta_0)}, \tag{5}$$

respectively. Note that here the lifetime of a droplet is defined to be the time it takes for it to evaporate entirely (*i.e.* the time it takes for V to reach zero) and has been scaled with an appropriate reference timescale $\rho(3V_0/2\pi)^{2/3}/2D(c_{\rm sat}-c_\infty)$. [Nguyen and Nguyen [4, Eq. (6)] and hence Nguyen and Nguyen [1] used essentially the same reference timescale as we do here, but introduced an insignificant error of less than 1% into their subsequent results by replacing $2^{5/3} \simeq 3.1831$ with $10/\pi \simeq 3.1748$.] Picknett and Bexon [2] showed that when the initial contact angle θ_0 is less than a relatively large critical value, denoted here by $\theta_{\rm crit}$, then $t_{\rm CA}(\theta_0)$ is greater than $t_{\rm CR}(\theta_0)$, and when θ_0 is greater then $\theta_{\rm crit}$, then $t_{\rm CA}(\theta_0)$ is slightly less than $t_{\rm CR}(\theta_0)$, but that the absolute difference between them is relatively small. Picknett and Bexon [2] used a polynomial approximation to the function $g(\theta)$, but using the exact expression (3) yields qualitatively similar results, and, in particular, shows that $\theta_{\rm crit} \simeq 2.5830$ (*i.e.* $\theta_{\rm crit} \simeq 148^\circ$).

However, as Picknett and Bexon [2] also showed, and as, for example, Bourgès-Monnier and Shanahan [5] subsequently described in greater detail, droplet evaporation can also occur in a variety of more complicated modes in which, in general, both the contact radius R and the contact angle θ vary. A variety of such modes have been identified experimentally, but probably the simplest is the combined pinned-receding mode considered by Nguyen and Nguyen [1] in which initially the contact line is pinned but subsequently it de-pins and recedes. Specifically, for initial contact angles θ_0 less than or equal to a so-called transition contact angle θ^* (*i.e.* satisfying $0 \le \theta_0 \le \theta^*$) the contact line is always de-pinned and the droplet always evaporates according to the CA mode; however, for initial contact angles θ_0 greater than the transition contact angle θ^* (*i.e.* satisfying $\theta_0 > \theta^*$) the contact line is initially pinned and so initially the droplet evaporates according to the CR mode, but when θ decreases to θ^* the contact line de-pins and thereafter the droplet evaporates according to the CA mode. The scaled lifetime of a droplet evaporating in the combined pinned-receding mode is denoted by $\tau = \tau(\theta_0, \theta^*)$. Unlike $t_{\rm CR}$ and $t_{\rm CA}$, τ is, in general, a function of the transition contact angle θ^* as well as of the initial contact angle θ_0, and will not, in general, be equal to either $t_{\rm CR}$ or $t_{\rm CA}$ when $\theta_0 > \theta^*$. Specifically, for $0 \le \theta_0 \le \theta^*$ we have $\tau = t_{\rm CA}$, where $t_{\rm CA}$ is given by (5), but for $\theta_0 > \theta^*$ we have

$$\tau = \left(\frac{2(1+\cos\theta_0)^2}{\sin\theta_0(2+\cos\theta_0)}\right)^{2/3}\left[\int_{\theta^*}^{\theta_0}\frac{2\,\mathrm{d}\theta}{g(\theta)} + \frac{\sin\theta^*(2+\cos\theta^*)}{g(\theta^*)}\right]. \tag{6}$$

Note that in the special case $\theta^* = 0$ we recover the lifetime of the constant radius mode $\tau(\theta_0, 0) \equiv t_{\mathrm{CR}}(\theta_0)$ and that in the special case $\theta^* = \theta_0$ we recover the lifetime of the constant angle mode $\tau(\theta_0, \theta_0) \equiv t_{\mathrm{CA}}(\theta_0)$.

Nguyen and Nguyen [1] state that "the lifetime of droplets evaporating by the combined pinned-receeding mode is bounded by the lifetimes of the single pinned mode (the lower limit) and single receding mode (the upper limit)", and write (expressed in their notation in their equation (5)) that $t_{\mathrm{CR}} \leq \tau \leq t_{\mathrm{CA}}$. Evidently their equation (5) cannot be true for all values of θ_0, since, as we have already seen, $t_{\mathrm{CA}} < t_{\mathrm{CR}}$ for $\theta_0 > \theta_{\mathrm{crit}}$, but it is true for the restricted range of values of θ_0 considered in the remainder of the present Comment, namely $0 \leq \theta_0 \leq \pi/2$. Notwithstanding this, Nguyen and Nguyen [1] used a rational approximation to the function $g(\theta)$ to draw a "master diagram" (their Figure 2) which they observe shows that "the lifetime of the combined pinned-receding mode is located outside the confined area between the two limit lines" and, in particular, that "there are many "transition" lines for the combined mode, located above the lifetime line of the single receding mode", both of which statements appear to contradict their earlier statement that $t_{\mathrm{CR}} \leq \tau \leq t_{\mathrm{CA}}$. This apparent contradiction arises because in their master diagram Nguyen and Nguyen [1] plotted t_{CR} and t_{CA} as functions of the initial contact angle θ_0 but plotted τ as a function of the transition contact angle θ^* for several values of θ_0. To clarify matters (and, in particular, to show that there is in fact no contradiction between their statements) Figure 1 shows a new version of their master diagram in which t_{CR}, t_{CA} and τ are *all* plotted as functions of the initial contact angle θ_0 for $0 \leq \theta_0 \leq \pi/2$, the latter for several values of the transition contact angle θ^*. In particular, Figure 1 shows that for every value of θ^* in the range $0 \leq \theta^* \leq \pi/2$, $\tau = t_{\mathrm{CA}}$ for $0 \leq \theta_0 \leq \theta^*$ and $t_{\mathrm{CR}} < \tau < t_{\mathrm{CA}}$ for $\theta^* < \theta_0 \leq \pi/2$. Hence, at least for the range of values of θ_0 shown, Figure 1 confirms the tentative suggestion by Shanahan *et al.* [6] that the transition curve lies between the curves corresponding to t_{CR} and t_{CA} and, in particular, shows that τ is always greater than t_{CR} and less than or equal to t_{CA}. In other words, Figure 1 shows that, at least for droplets with initial contact angles that are less than or equal to 90°, the lifetime of a droplet evaporating in the constant angle mode is always longer than of equal to that of a droplet with the same initial shape and volume evaporating in the combined pinned-receding mode, which is itself always longer than that of a droplet with the same initial shape and volume evaporating in the constant radius mode. Furthermore, Figure 1 shows that in the limit of small transition contact angle, $\theta^* \to 0^+$, the curve corresponding to $\tau(\theta_0, \theta^*)$ approaches the curve corresponding to $t_{\rm CR}(\theta_0)$ from above for all values of θ_0 according to $\tau = t_{\rm CR}(\theta_0) + O(\theta^*)$, while in the limit $\theta^* \to \pi/2^-$ it is equal to $t_{\rm CA}(\theta_0)$ for all θ_0 except in the vanishingly small range $\theta^* < \theta_0 \leq \pi/2$ in which it approaches the maximum value of $t_{\rm CA}(\theta_0)$, namely $t_{\rm CA}(\pi/2) = 1$, from below according to $\tau = 1 - O\left((\pi/2) - \theta^*\right)^2$. Figure 1 also shows that in the limit of small initial contact angle, $\theta_0 \to 0^+$, $t_{\rm CR}$, $t_{\rm CA}$ and τ all approach zero like $O(\theta_0^{1/3})$, and for all values of θ^* satisfying $0 \leq \theta^* \leq \pi/2$ the curve corresponding to $\tau(\theta_0, \theta^*)$ departs from the curve corresponding to $t_{\rm CA}(\theta_0)$ at $\theta_0 = \theta^*$ with zero slope and positive curvature according to $\tau = t_{\rm CA}(\theta^*) + O(\theta_0 - \theta^*)^2$. Finally, it is important to note that Figure 1 confirms the conclusions of Nguyen and Nguyen [1] that "there are many "transition" lines for the combined mode" and that they have a qualitatively different shape from that tentatively suggested by Shanahan *et al.* [6].

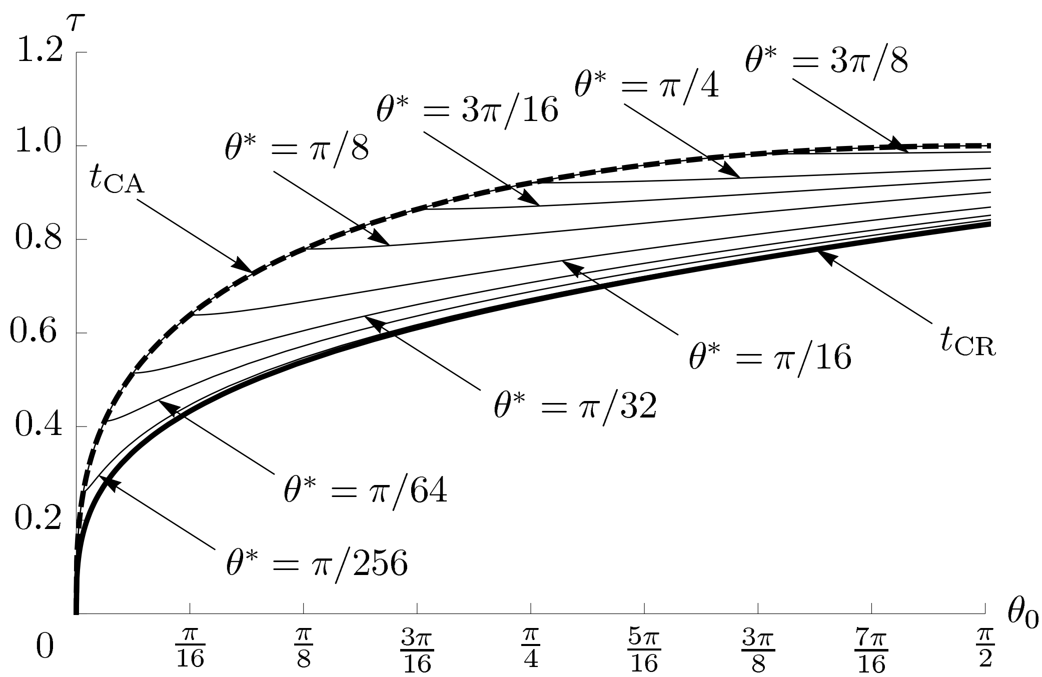

Figure 1: The scaled lifetime of a droplet evaporating in the combined pinned-receding mode, $\tau = \tau(\theta_0, \theta^*)$, plotted as a function of the initial contact angle θ_0 for $0 \leq \theta_0 \leq \pi/2$ for several values of the transition contact angle $\theta^* = \pi/256$, $\pi/64$, $\pi/32$, $\pi/16$, $\pi/8$, $3\pi/16$, $\pi/4$, $3\pi/8$ and $\pi/2$ [in which case τ coincides with $t_{\rm CA}$]. Also shown are the scaled lifetimes of a droplet evaporating in the constant radius mode, $t_{\rm CR}(\theta_0)$, given by (4) (shown with the thick solid line), and of a droplet evaporating in the constant angle mode, $t_{\rm CA}(\theta_0)$, given by (5) (shown with the thick dashed line).

References

[1] Nguyen, T.A.H.; Nguyen, A.V. Increased evaporation kinetics of sessile droplets by using nanoparticles. *Langmuir* **2012**, *28*, 16725–16728.

[2] Picknett, R.G.; Bexon, R. The evaporation of sessile or pendant drops in still air. *J. Coll. Int. Sci.* **1977**, *61*, 336–350.

[3] Popov, Y.O. Evaporative deposition patterns: Spatial dimensions of the deposit. *Phys. Rev. E* **2005**, *71*, 036313.

[4] Nguyen, T.A.H.; Nguyen, A.V. On the lifetime of evaporating sessile droplets. *Langmuir* **2012**, *28*, 1924–1930.

[5] Bourgès-Monnier, C.; Shanahan, M.E.R. Influence of evaporation on contact angle. *Langmuir* **1995**, *11*, 2820–2829.

[6] Shanahan, M.E.R.; Sefiane, K.; Moffat, J.R. Dependence of volatile droplet lifetime on the hydrophobicity of the substrate. *Langmuir* **2011**, *27*, 4572–4577.