Advances in Colloid and Interface Science 243 (2017) 121–128

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Resolving an ostensible inconsistency in calculating the evaporation rate of sessile drops

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ARTICLE INFO

Keywords:
Evaporation
Sessile drops
Micro-liter drops
Electrostatic analogy
Evaporation flux variation
Diffusion

ABSTRACT

This paper resolves an ostensible inconsistency in the literature in calculating the evaporation rate for sessile drops in a quiescent environment. The earlier models in the literature have shown that adapting the evaporation flux model for a suspended spherical drop to calculate the evaporation rate of a sessile drop needs a correction factor; the correction factor was shown to be a function of the drop contact angle, i.e. $\boldsymbol{f}(\boldsymbol{\theta})$. However, there seemed to be a problem as none of the earlier models explicitly or implicitly mentioned the evaporation flux variations along the surface of a sessile drop. The more recent evaporation models include this variation using an electrostatic analogy, i.e. the Laplace equation (steady-state continuity) in a domain with a known boundary condition value, or known as the Dirichlet problem for Laplace's equation. The challenge is that the calculated evaporation rates using the earlier models seemed to differ from that of the recent models (note both types of models were validated in the literature by experiments). We have reinvestigated the recent models and found that the mathematical simplifications in solving the Dirichlet problem in toroidal coordinates have created the inconsistency. We also proposed a closed form approximation for $\boldsymbol{f}(\boldsymbol{\theta})$ which is valid in a wide range, i.e. $8^\circ \le \boldsymbol{\theta} \le 131^\circ$. Using the proposed model in this study, theoretically, it was shown that the evaporation rate in the CWA (constant wetted area) mode is faster than the evaporation rate in the CCA (constant contact angle) mode for a sessile drop.

1. Introduction

Evaporation of micro-liter drops at room temperature, normal atmospheric condition and in quiescent environment, is considered not to be limited by the transfer rate of molecules across the liquid-vapor interface (phase change), but by the transfer from the drop surface to the surrounding (vapor transport) [1]. Transport of vapor from drop surface to the surrounding may potentially be attributed to diffusion, convection, or both [2,3]. Solving the mass balance equations, Langmuir [4] showed for micro-liter drops, assuming a pure-convective driven evaporation results in a linear relationship between the evaporation flux and drop radius squared; while assuming a pure-diffusive driven evaporation results in a linear relationship between the evaporation flux and drop radius. As through experiments, Langmuir [4] and proceeding researchers observed the latter case, they came to the conclusion that evaporation of a non-volatile micro-liter sessile drop in room temperature is governed by diffusion and not convection e.g. [2,3,5–11]. It was also assumed that such evaporation is a steady-state process. The steady-state and non-convective assumptions (i.e. Maxwell assumptions [12]) are widely used in literature for finding the evaporation rate of sessile drops [6,7,9,10,13–23]. As shown in our previous study [24], evaporation of micro-liter drops is neither steady-state, nor purely-diffusive, in general. As shown in [24], the error in using Maxwellian model depends on the value of $w_{v_{eq}}^\circ$ (ratio of molar vapor density to molar air-vapor mixture density in a vapor saturated air). It should be noted that for drops in this study the value of $w_{v_{eq}}^\circ$ is <0.01 which means using Maxwellian model results in $<1\%$ error in calculating the evaporation flux on the free surface of a suspended drop [24].

Adapting Maxwellian models to sessile drops, but for now ignoring the solid substrate effect (i.e. evaporation flux on free surface of a sessile drop is assumed equal to the evaporation flux of a suspended drop with an equal radius of curvature), and knowing that the surface area of a spherical cap drop (S) can be calculated as $\frac{2\pi a^2}{1+\cos\theta}$, the total evaporation from a sessile drop (J) would be [21]:

$$J = \rho_L^\circ \frac{\partial V}{\partial t} = J_{\boldsymbol{v}}^\circ . S = -2\pi a \rho^\circ D \left(w_{v_{eq}}^\circ - w_{v_\infty}^\circ \right) \frac{\sin\theta}{1+\cos\theta} \qquad (1)$$

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http://dx.doi.org/10.1016/j.cis.2016.05.015

where $\rho_L^{\diamond}$ is the liquid molar density $({}^{\mathrm{mol}}/_{\mathrm{m}^3})$; V is the drop volume (m^3); t is time (s); $J_v^{\diamond}$ is the molar flux of vapor $({}^{\mathrm{mol}}/_{\mathrm{m}^2\cdot\mathrm{s}})$; S is drop surface area (m^2); a is the drop wetted contact radius (m); $\rho^{\diamond}$ is the molar density of air-vapor mixture $({}^{\mathrm{mol}}/_{\mathrm{m}^3})$; D is the binary diffusion constant of vapor into air $({}^{\mathrm{m}^2}/_{\mathrm{s}})$; $w_{v_{eq}}^{\diamond}$ and $w_{v_\infty}^{\diamond}$ are $\rho_v^{\diamond}/\rho^{\diamond}$ in a thin shell surrounding the liquid and at far afield, respectively; $\rho_v^{\diamond}$ is the molar density of vapor $({}^{\mathrm{mol}}/_{\mathrm{m}^3})$, and θ is the drop's contact angle. It can be assumed that $w_{v_{eq}}^{\diamond}$ is equal to the density ratio of vapor to air-vapor mixture in a vapor saturated air [25].

It is argued that the presence of a solid substrate changes the evaporation rate values from Maxwellian models (e.g. [10,20]) by $f(\theta)$, see Eq. (2).

$$J = \rho_L^{\diamond}\frac{\partial V}{\partial t} f(\theta) = J_{\boldsymbol{v}}^{\diamond}.Sf(\theta) = -2\pi a\rho^{\diamond} D\left(w_{v_{eq}}^{\diamond} - w_{v_\infty}^{\diamond}\right)\frac{\sin\theta}{1+\cos\theta} f(\theta) \tag{2}$$

Literature studies have used different approaches for finding the value of $f(\theta)$, e.g. differential mass balance [9,21], transforming into an electrostatic problem [20], or fitting experimental values [26]. Picknett and Bexon [20] is the only study in the literature which provides an exact solution for $f(\theta)$. They solved an electrostatic analogy (evaluating the capacitance of an isolated conducting body with the same size and shape as a drop) using Snow's series solution, and showed that in presence of a solid substrate evaporation rate changes as [20]:

$$f(\theta)_{Picknett\ \&\ Bexon} = \begin{cases} \dfrac{0.6366\left(\dfrac{\pi\theta}{180}\right) + 0.09591\left(\frac{\pi\theta}{180}\right)^2 - 0.06144\left(\frac{\pi\theta}{180}\right)^3}{1-\cos\theta}, & 0 \le \theta < 10^\circ \\ \dfrac{0.00008957 + 0.6333\left(\dfrac{\pi\theta}{180}\right) + 0.1160\left(\frac{\pi\theta}{180}\right)^2 - 0.08878\left(\frac{\pi\theta}{180}\right)^3 + 0.01033\left(\frac{\pi\theta}{180}\right)^4}{1-\cos\theta}, & 10^\circ \le \theta \le 180^\circ \end{cases} \tag{3}$$

where θ is in degrees, and the total evaporation rate (J) can be found by substituting Eq. (3) for $f(\theta)$ in Eq. (2). For other approximate relations for $f(\theta)$ see [9,10,21]. Note that in [20] or other studies mentioned above, there was no explicit reference to variation of evaporation flux along the surface of a sessile drop; $f(\theta)$ was thought of a term to modify the total evaporation rate while evaporation flux was deemed uniform along the drop free surface (similar to a suspended spherical drop).

A number of studies, starting approximately 15 years ago, found or argued that for sessile drops, the evaporation flux changes from a maximum value at the contact line to a minimum value at the drop apex, see Fig. 1, e.g. [27–36]. In the meantime, many have tried to capture this variation and include it into their evaporation models. The problem here is that the recent models which capture the evaporation variation along the drop surface (e.g. [35]) provide results which are inconsistent with Eqs. (2) and (3) (e.g. older models given in [20]). This has divided the literature into two streams, and of course the majority of these works support the recent models (e.g. in [28,29]), with the logic that the evaporation flux variation was not explicitly mentioned in the early literature models e.g. [20]. The aim of this paper is to investigate the cause(s) that have created the inconsistencies between the modeling approaches in the literature.

Models which quantify the evaporation variation along the drop surface are based on electrostatic analogies (see Appendix I). In electrostatic analogies, the vapor concentration and evaporation flux are related to electrostatic potential and electrostatic field, respectively [35]. The two types of electrostatic analogy found in literature are: (i) the problem of finding the electrostatic fields and charge densities in two-dimensional corners and along the edges [37], and (ii) the Dirichlet problem for a domain bounded by two intersecting spheres, or capacitance of an equiconvex lens [38].

The first electrostatic analogy (mentioned in [36]) is for flat conducting surfaces. As such, its use is limited to small contact angles, i.e. when the drop surface is nearly flat. The second electrostatic analogy (used in [2,3,27–35,39]) is valid for spherical cap geometries. The spherical cap geometry is not a major limitation for small drops (<2 mm), since drops smaller than 2 mm have spherical cap shape (capillary length for pure water at standard temperature and pressure is approximately 2 mm). As such, the Dirichlet analogy is an appropriate analogy for the evaporation of micro-liter sessile drops. This analogy problem is relatively complicated [38] and so far, it has been solved with some approximations and simplifications e.g. [35] or [41]. For example, Popov [41] solved the electrostatic analogy assuming that the contact line of the drop remains pinned during the evaporation, the initial contact angle is small, and the contact angle linearly decreases in time.

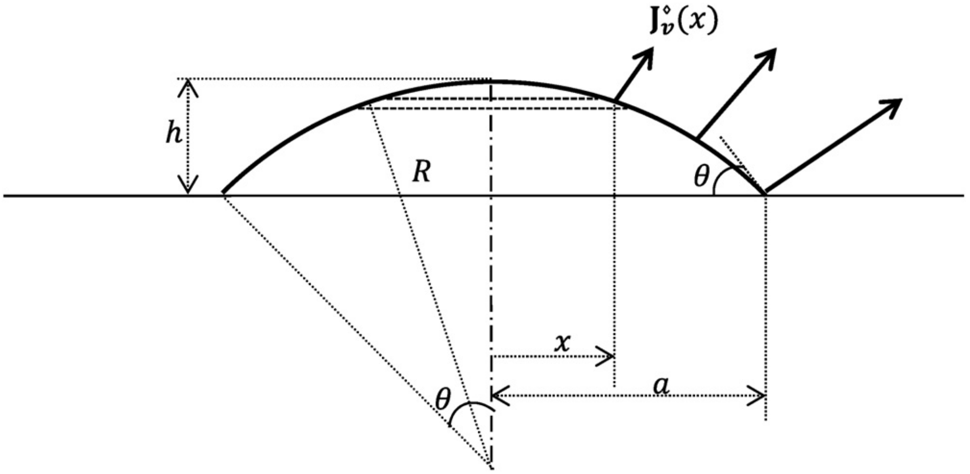

Fig. 1. Variation of evaporation flux along the drop surface is shown. $J_v^{\diamond}(x)$ is the evaporation flux at x. Evaporation flux is at its maximum at the contact line. It is assumed that a drop has a spherical cap shape with radius R.