Appendix

Analytical Solution of Diffusive Evaporation for Sessile Drops

We find that there are many errors and inconsistent (often confusing) results obtained for the evaporation of the sessile droplets and reported in the literature that have been obtained from the Lebedev solutions for electrostatic field around a lens-shaped conductor (Lebedev, 1965). Therefore, here we wish to re-establish the self-consistent correct analytical solution for the diffusive flux, which is the key to the analysis of this paper.

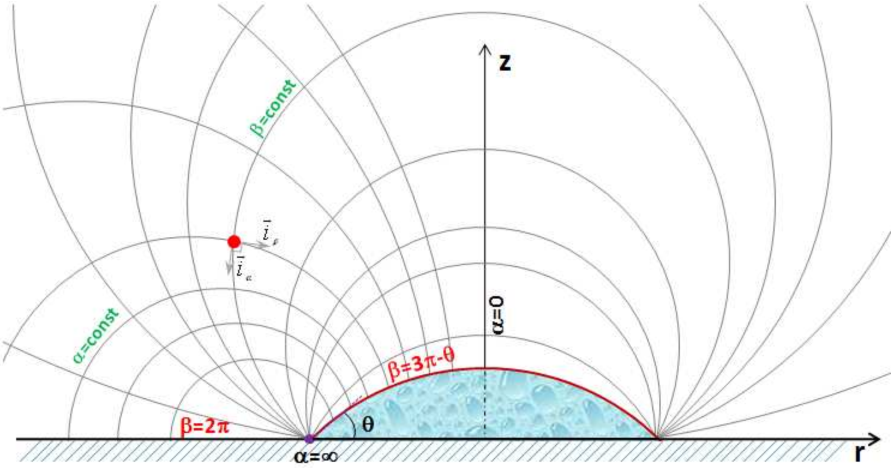

Figure 1A. Schematic of a sessile droplet with the shape of spherical cap on a flat surface in the rotationally symmetric cylindrical (r, z) and toroidal (α, β) coordinate systems.

We consider the sessile drop having a shape of spherical cap which is rotationally symmetric about the direction of gravity and can be described using the rotationally symmetric cylindrical coordinates (r, z), where the cylindrical (longitudinal) axis, *z*, is identical to the direction of gravity, and the origin and the polar axis, *r*, lie on the solid-fluid planar (reference) interface (Figure 1A). The diffusive evaporation of the sessile droplet can be tractably solved using the reduced toroidal coordinates (α, β), which are related with the cylindrical coordinates as follows:

$$r = \frac{R \sinh \alpha}{\cosh \alpha - \cos \beta} \tag{A1}$$

$$z = \frac{R \sin \beta}{\cosh \alpha - \cos \beta} \tag{A2}$$

where R is the contact radius of the droplet with the solid surface. The solid-vapour and liquid-vapour interfaces are described by $\beta = 2\pi$ and $\beta = 3\pi - \theta$, where θ is the contact angle between the liquid-vapour and solid-vapour interfaces as measured through the liquid phase. The physical domain of the vapour phase is limited by $\infty > \alpha \geq 0$ and $3\pi - \theta \geq \beta \geq 2\pi$.

The second Fick law describes the mass conservation for the vapour evaporation by diffusion. The time scale analysis indicates that the evaporation can be described by the quasi-steady state with the transient term in the Fick law being neglected, yielding the Laplace equation, $\nabla^2 C = 0$, for the vapor concentration, C, which in the toroidal coordinate system reduces to [1]

$$\frac{\partial}{\partial \alpha}\left(\frac{\sinh\alpha}{\cosh\alpha - \cos\beta}\frac{\partial C}{\partial \alpha}\right) + \frac{\partial}{\partial \alpha}\left(\frac{\sinh\alpha}{\cosh\alpha - \cos\beta}\frac{\partial C}{\partial \beta}\right) = 0 \tag{A3}$$

Far away from the droplet surface C is equal to the vapour concentration, C_∞, in the ambient environment. Substituting $C = \sqrt{2\cosh\alpha - 2\cos\beta}\; A(\alpha)B(\beta) + C_\infty$ into Eq. (A3) yields the separable differential equations as

$$\frac{1}{A\sinh\alpha}\frac{d}{d\alpha}\left(\sinh\alpha\frac{dA}{d\alpha}\right) + \frac{1}{4} = -\frac{d^2B}{Bd\beta^2} = -\tau^2 = const \tag{A4}$$

The minus sign before τ is chosen for the physical consistence of the evaporation considered.

The particular solutions for $A(\beta)$ are the Legendre functions of the first kind, $P_{i\tau-1/2}(\cosh\alpha)$, and of the second kind, $Q_{i\tau-1/2}(\cosh\alpha)$, where $i = \sqrt{-1}$. However, to avoid a divergence on the z-axis, i.e., when $\alpha \to 0$, the $Q_{i\tau-1/2}(\cosh\alpha)$ solutions must be discarded because $Q_{i\tau-1/2}(1) \to \infty$. The particular solutions for $B(\beta)$ can be described as $B_\tau(\beta) = M_\tau \cosh\tau\beta + N_\tau \sinh\tau\beta$. The boundary condition of zero net of the diffusive flux, $\vec{J} = -D\nabla C$, on the solid-vapour interface requires $dB/d\beta = 0$ at $\beta = 2\pi$, which gives $M_\tau \sinh 2\pi\tau + N_\tau \cosh 2\pi\tau = 0$. Finally, the solution for the vapour concentration around the sessile drop can conveniently be described as

$$C = (C_s - C_\infty)\sqrt{2\cosh\alpha - 2\cos\beta}\int_0^\infty E_\tau P_{i\tau-1/2}(\cosh\alpha)\cosh\left[(2\pi-\beta)\tau\right]d\tau + C_\infty \tag{A5}$$

where E_τ is the integration constant and C_s is the (saturation) vapour concentration at the droplet interface. The integration constant can be determined from the boundary condition, $C = C_s$, at the droplet surface, giving

$$\frac{1}{\sqrt{2\cosh\alpha + 2\cos\theta}} = \int_0^\infty E_\tau P_{i\tau-1/2}\left(\cosh\alpha\right)\cosh\left[\left(\pi-\theta\right)\tau\right]d\tau \tag{A6}$$

Applying the Mehler-Fock integral transform [2] and solving Eq. (A6) for E_τ give

$$E_\tau = \frac{\tau\tanh\pi\tau}{\cosh\left[\left(\pi-\theta\right)\tau\right]}\int_1^\infty \frac{P_{i\tau-1/2}\left(x\right)}{\sqrt{2x+2\cos\theta}}dx \tag{A7}$$

The integral on the RHS of Eq. (A7) can be analytically integrated, giving

$$E_\tau = \frac{\cosh\tau\theta}{\cosh\tau\pi\cosh\left[\left(\pi-\theta\right)\tau\right]} \tag{A8}$$

Inserting Eq. (A8) into Eq. (A5) yields the following prediction for the scaled concentration:

$$C = \left(C_s - C_\infty\right)\sqrt{2\cosh\alpha - 2\cos\beta}\int_0^\infty P_{i\tau-1/2}\left(\cosh\alpha\right)\frac{\cosh\tau\theta\cosh\left[\left(2\pi-\beta\right)\tau\right]}{\cosh\tau\pi\cosh\left[\left(\pi-\theta\right)\tau\right]}d\tau + C_\infty \tag{A9}$$

The net, J, of the diffusive flux at the droplet surface depends on the toroidal coordinate α and can be determined as

$$J\left(\alpha\right) = \left(-D\nabla C\cdot\vec{i}_\beta\right)_{\beta=3\pi-\theta} = \frac{\cosh\alpha+\cos\theta}{R/D}\left(\frac{\partial C}{\partial\beta}\right)_{\beta=3\pi-\theta} \tag{A10}$$

where $\vec{i}_\beta$ is the unit vector along the β-direction (Figure 1A). Inserting Eq. (A9) into Eq. (A10) gives

$$J\left(\alpha\right) = \frac{C_s - C_\infty}{R/D}\left\{\frac{\sin\theta}{2} + \sqrt{2}\left(\cosh\alpha+\cos\theta\right)^{3/2}\int_0^\infty \frac{\tau\cosh\theta\tau}{\cosh\pi\tau}\tanh\left[\tau\left(\pi-\theta\right)\right]P_{i\tau-1/2}\left(\cosh\alpha\right)\,d\tau\right\} \tag{A11}$$

It is noted that the numerical factor of $\sqrt{2}$ in the front of the integral on the right-hand side of Eq. (A11) is missing in some papers, e.g. [3]. Eq. (A11) also indicates that the diffusive flux changes with α and is not constant along the droplet surface if the contact angle is not the right angle. For $\theta = \pi / 2$, Eq. (A11) can be further simplified to give $J_0 = J(\alpha, \theta = \pi / 2) = D(C_s - C_\infty) / R$, which shows that the diffusive flux is constant along the droplet surface.

References

1. Lebedev, N. N., Special functions and their applications. *Revised English ed., Chapter 7 and 8 (Prentice-Hall, Englewood Cliffs)* **1965**.
2. Polyanin, A. D.; Manzhirov, A. V., *Handbook of integral equations*. Chapman & Hall/CRC: Boca Raton, FL, USA, **2008**; p 1108.
3. Hu, H.; Larson, R. G., Evaporation of a Sessile Droplet on a Substrate. *The Journal of Physical Chemistry B* **2002,** 106, (6), 1334-1344.