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Letter

Lifetime of evaporating two-dimensional sessile droplets

Ehud Yariv
Department of Mathematics, Technion–Israel Institute of Technology, Haifa 32000, Israel

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Prevailing diffusion-limited analyses of evaporating sessile droplets are facilitated by a quasisteady model for the evolution of vapor concentration in space and time. When attempting to employ that model in two dimensions, however, one encounters an impasse: the logarithmic growth of concentration at large distances, associated with the Green's function of Laplace's equation, is incompatible with the need to approach an equilibrium concentration at infinity. Observing that the quasisteady description breaks down at large distances, the diffusion problem is resolved using matched asymptotic expansions. Thus the vapor domain is conceptually decomposed into two asymptotic regions: one at the scale of the drop, where vapor transport is indeed quasisteady, and one at a remote scale, where the drop appears as a point singularity and transport is genuinely unsteady. The requirement of asymptotic matching between the respective regions furnishes a self-consistent description of the time-evolving evaporation process. Its solution provides the droplet lifetime as a universal function of a single physical parameter. Our scheme avoids the use of a remote artificial boundary, which introduces a nonremovable dependence upon a nonphysical parameter.

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Introduction. The evaporation of sessile droplets plays a role in numerous physical and technological fields and has been actively investigated for decades [1]. Often, the quantity of interest is the lifetime of the droplet—the time it takes to evaporate completely from a specified initial geometry [2,3]. In modeling drop evaporation, a natural idealization is that of a semibounded vapor domain, with an equilibrium concentration specified at infinity. Modeling is significantly simplified by identifying the rate limiting processes [4], with the most common description postulating diffusion-limited transport [5–7]. With the atmosphere at the drop boundary assumed saturated with vapor, the evaporation process is completely described by diffusive transport, driven by the difference between the saturation and equilibrium concentrations. Due to the large disparity between that difference and the liquid-drop density, the diffusive process is quasisteady, with the diffusion equation approximated by Laplace's equation.

While prevailing configurations are obviously three-dimensional (3D), there is an interest in the companion 2D problem, where advanced mathematical methods (e.g., conformal maps) may provide useful insight [8]. The use of idealized 2D models goes back to Yarin *et al.* [9] who, following Deegan *et al.* [10,11], analyzed deposit patterns in evaporating droplets. Making use of their amenity to analytic methods, 2D configurations have been employed to investigate interactions between neighboring droplets [8]—a challenging contemporary research area [12,13]. Recently, a 2D model was used for studying the effect of chemically patterned substrates [14].

Unfortunately, these efforts have been frustrated by an inherent incompatibility of Laplace's equation in 2D. Indeed, with a finite vapor flux emanating from the drop, the vapor concentration approaches a sourcelike behavior at large distances. With the associated logarithmic growth, it is impossible to approach the uniform equilibrium concentration at infinity. As a remedy, it has been common [8,9,14] to replace the condition at infinity by an alternative condition at an artificial remote boundary, effectively rendering the vapor domain bounded. This procedure, however, introduces a superfluous dependence upon the distance to the remote boundary that does not disappear at any later stage (as is evident by the underlying logarithmic growth in the original unbounded domain). One may claim that the calculated quantities of interest may still exhibit the correct qualitative dependence upon the remaining (physically meaningful) parameters of the problem. That said, we cannot avoid the discomfort which follows from a persistent dependence upon a nonphysical parameter—a dependence which, in a sense, undermines the very premise underlying the use of 2D models at the first place.

In this Letter we propose a resolution of the problem, based upon the observation that the quasisteady approximation, which holds in the vicinity of the drop, breaks down at large distances away from it. At these distances, where the diffusion equation cannot be approximated by Laplace's equation, the drop appears as a point singularity. The separate solutions in the two regions are linked using the method of matched asymptotic expansions [15]. With the goal of presenting the simplest possible calculation that nonetheless exhibits the key physical features, we employ the "constant-radius" model [5], where the drop base is fixed while the contact angle instantaneously adjusts to the time-evolving area.

Problem formulation. A 2D droplet (density ρ) is placed upon an infinite substrate. The drop base is $2a$ and the initial contact angle is α_0. The drop evaporates by a diffusive process, with a uniform vapor diffusivity D. At the drop boundary, the vapor concentration is set to the saturation concentration c_{sat}; at large distances it approaches the equilibrium concentration c_∞. Assuming that a is small compared with

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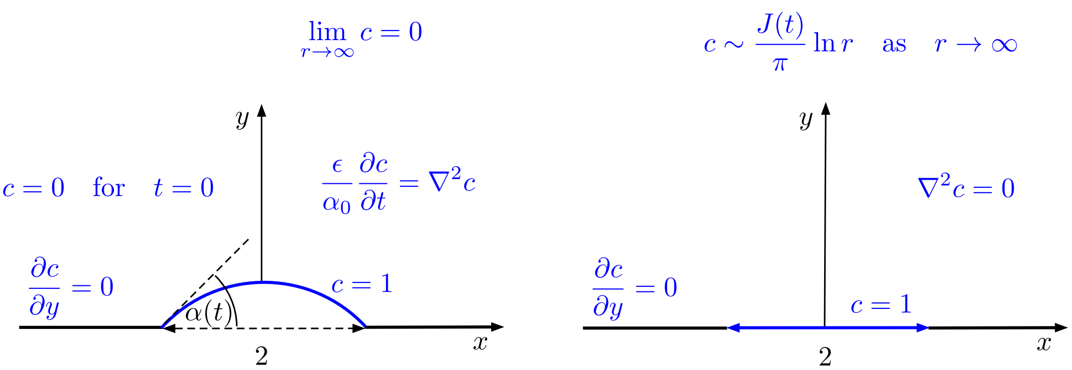

FIG. 1. (a) Dimensionless geometry, with a description of the diffusion-limited problem. (b) An approximate quasisteady description for thin droplets.

the capillary length, capillarity dominates the shape of the free surface, which is therefore of uniform curvature. In the above description, evaporation is animated by the difference $\Delta c = c_{\text{sat}} - c_\infty$. We similarly define $\Delta\rho = \rho - c_\infty$.

We employ a dimensionless notation where length variables are normalized by a, the time t by $a^2\alpha_0\Delta\rho/D\Delta c$, the concentration c (measured relative to c_∞) by Δc, and the mass flux (per unit length) J by $D\Delta c$. We use Cartesian coordinates (x, y), with the x axis coinciding with the substrate and the y axis bisecting the drop, with vapor transport taking place for $y > 0$, outside the drop. In that domain, the excess concentration c is governed by (i) the diffusion equation,

$$\frac{\epsilon}{\alpha_0}\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}, \tag{1}$$

where $\epsilon = \Delta c/\Delta\rho$, (ii) the initial condition, $c = 0$ for $t = 0$, (iii) the saturation condition, $c = 1$ at the circular-arc boundary, (iv) the no-flux condition,

$$\frac{\partial c}{\partial y} = 0 \quad \text{on } y = 0 \text{ for } |x| > 1, \tag{2}$$

and (v) the decay condition, $\lim_{r\to\infty} c = 0$, where $r = \sqrt{x^2 + y^2}$. The dimensionless geometry and diffusion-limited problem are described in Fig. 1(a).

For a given distribution of c, the instantaneous mass flux $J(t)$ may be determined as an integral of $\partial c/\partial n$ over the drop boundary. For a given $J(t)$, the drop evolves according to the global balance,

$$\alpha_0 J(t) + (1 - \epsilon)\frac{dA}{dt} = 0, \tag{3}$$

wherein A is the drop area (normalized by a^2). With the drop boundary constrained to a circular arc of base 2, an (instantaneous) contact angle α uniquely sets the area as

$$A(\alpha) = \frac{2\alpha - \sin 2\alpha}{2\sin^2\alpha}. \tag{4}$$

The lifetime T is therefore obtained by integration of (3) subject to the initial condition $\alpha(0) = \alpha_0$ and the final condition $\alpha(T) = 0$, giving

$$\alpha_0 \int_0^T J(t)\,dt = (1 - \epsilon)A(\alpha_0). \tag{5}$$

Quasisteady transport from thin droplets. Since the liquid density is much larger than the vapor concentration in all realistic scenarios, ϵ is exceedingly small. The diffusion equation (1) degenerates to Laplace's equation. The vapor transport becomes quasisteady, with the time t entering as a parameter.

Assuming further a thin droplet [16–19] we are naturally led to the limit

$$\epsilon \ll \alpha_0 \ll 1, \tag{6}$$

where the quasisteady approximation remains valid. The focus on thin droplets results in the following useful simplifications. First, to leading order, the drop boundary coincides with the segment $(-1, 1)$ on the x axis. The saturation condition thus becomes

$$c = 1 \quad \text{for } |x| < 1 \text{ at } y = 0. \tag{7}$$

Second, since the drop shape does not affect the transport problem, the flux $J(t)$ is independent of the instantaneous contact angle $\alpha(t)$. Third, as $\alpha(t) < \alpha_0$, the droplet area is $O(\alpha_0)$. Specifically, we observe from (4) that $A(\alpha) \sim 2\alpha/3$. The global balance (5) readily yields

$$\int_0^T J(t)\,dt = \frac{2}{3}, \tag{8}$$

where the dependence upon α_0 enters only through $J(t)$. The simplified form (8) justifies the choice of the normalizing time scale. The quasisteady description for thin droplets is illustrated in Fig. 1(b).

Quasisteady analysis. With a nonzero flux J and the no-flux condition (2), Laplace's equation implies that

$$c \sim -\frac{J(t)}{\pi}\ln r \quad \text{as } r \to \infty. \tag{9}$$

Thus it is impossible to satisfy the far-field decay. This is the familiar obstacle in 2D analyses.

At this point we depart from previous investigations. Thus, instead of introducing an artificial remote boundary, we employ the method of matched asymptotic expansions [15], conceptually decomposing the vapor domain into two asymptotic regions. The first is at the scale of the drop, where the quasisteady description is valid, and the second at appropriate large distances (to be specified soon). With that approach, the decay condition is inapplicable on the drop scale, so no incompatibility arises.

The quasisteady problem thus consists of Laplace's equation, the saturation condition (7), and the no-flux condition (2). These constitute a *homogeneous* problem for $c' = c - 1$. It follows that c' is defined to within a multiplicative constant, which may be identified with the flux $J(t)$. For convenience, we shall temporarily regard (9) as an imposed (inhomogeneous) condition, which will uniquely determine c' for a given $J(t)$. The problem governing c' is formulated in the upper-half xy plane. To solve it, we form an odd extension of c' about the x axis. As Laplace's equation is invariant under such an extension, we are led to a problem governing c' in the entire plane. Since the homogeneous Dirichlet condition associated with (7) is trivially satisfied, the only remaining condition at $y = 0$ is the Neumann condition (2), which also applies to c'. Condition (9) now implies $c' \sim \mp\pi^{-1}J(t)\ln r$ as $y \to \pm\infty$.

The resulting problem is analogous to that governing the velocity potential of 2D irrotational flow through an aperture [20]. The solution is best described in the complex plane. Thus, writing $c' = \mathrm{Re}\{\phi(z)\}$, where $z = x + iy$ and ϕ is an analytic function, we find that $\phi(z)$ is given by the implicit relation

$$z = \cosh\frac{\pi\phi}{J(t)}. \tag{10}$$

For the purpose of asymptotic matching with the remote region, all we need is the local inversion of (10) as $\mathrm{Im}\{z\} \to \infty$, $\phi \sim -\pi^{-1}J(t)\ln(2z)$, where the asymptotic error is algebraically small. Forming the real part of that inversion provides the requisite refinement of (9),

$$c \sim 1 - \frac{J(t)}{\pi}\ln(2r) \quad \text{as } r \to \infty\ (y > 0). \tag{11}$$

As anticipated, the drop-scale solution, and in particular its large-r asymptotic behavior (11), are defined up to the unknown flux $J(t)$. This flux is set by the requirement of far-field decay, which so far has not been implemented. To that end, we consider now the remote transport.

Remote analysis. In what follows, we supplement the drop-scale solution by a comparable solution in a remote region. The extent of that region is determined from the approximation of (1) by Laplace's equation, based upon (6). The resulting quasisteady approximation clearly breaks down at distances of order $(\alpha_0/\epsilon)^{-1/2}$, where both sides of (1) become comparable.

We accordingly consider the unsteady transport at these remote distances. It is described using the stretched coordinate, $\tilde{r} = (\epsilon/\alpha_0)^{1/2}r$, with similar definitions of $\tilde{x}$ and $\tilde{y}$. Writing $c(x, y; t) = \tilde{c}(\tilde{x}, \tilde{y}; t)$, we see that at leading order $\tilde{c}$ is governed by the diffusion equation [cf. (1)]

$$\frac{\partial\tilde{c}}{\partial t} = \frac{\partial^2\tilde{c}}{\partial\tilde{x}^2} + \frac{\partial^2\tilde{c}}{\partial\tilde{y}^2}, \tag{12}$$

the initial condition, $\tilde{c} = 0$ at $t = 0$, and the decay condition, $\lim_{\tilde{r}\to\infty}\tilde{c} = 0$. Since the drop shrinks to the origin in the stretched coordinates, the no-flux condition (2) becomes

$$\frac{\partial\tilde{c}}{\partial\tilde{y}} = 0 \quad \text{on } \tilde{y} = 0 \text{ for } \tilde{x} \neq 0. \tag{13}$$

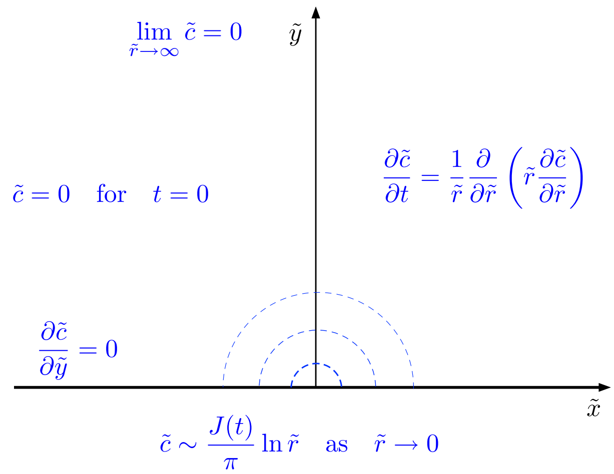

FIG. 2. Description of the remote problem governing $\tilde{c}(\tilde{r}; t)$.

The saturation condition does not apply. Rather, the singular behavior at the origin is set by asymptotic matching with (11), giving $\tilde{c} \sim -\pi^{-1}J(t)\ln\tilde{r}$ for $\tilde{r} \ll 1$. Since this inhomogeneous forcing is radially symmetric, we anticipate that so is $\tilde{c}$, whereby the no-flux condition (13) is trivially satisfied. The remote problem governing $\tilde{c}(\tilde{r}; t)$ is described in Fig. 2.

To solve the remote problem we employ the Laplace transform, generically defined by $\hat{f}(s) = \int_0^\infty f(t)e^{-st}\,dt$. Forming the transform of (12) gives, upon making use of the homogeneous initial condition and the radial symmetry,

$$s\hat{c} = \frac{1}{\tilde{r}}\frac{d}{d\tilde{r}}\left(\tilde{r}\frac{d\hat{c}}{d\tilde{r}}\right), \tag{14}$$

where $\hat{c}$ is the transform of $\tilde{c}$. This second-order equation must be solved subject to the decay requirement, $\hat{c}(\infty, s) = 0$. The solution is $\hat{c}(\rho, s) = A(s)K_0(s^{1/2}\tilde{r})$, wherein K_0 is the modified Bessel function of the second kind. Making use of the small-argument approximation of K_0 [21] gives

$$\hat{c}(\tilde{r}, s) \sim A(s)\left(\ln\frac{2}{s^{1/2}\tilde{r}} - \gamma_{\mathrm{E}}\right) \quad \text{for } \tilde{r} \ll 1, \tag{15}$$

where γ_{E} is the Euler-Mascheroni constant. Just as in (11), the asymptotic error is algebraically small.

Calculating the flux. Forming the transform of (11) gives $1/s - \hat{J}(s)\ln(2r)/\pi$, where $\hat{J}(s)$ is the transform of $J(t)$. Comparing with (15) we find that $A(s) = \hat{J}(s)/\pi$ and hence

$$\hat{J}(s) = \frac{\pi}{s}\left(\frac{1}{2}\ln\frac{16\alpha_0}{\epsilon s} - \gamma_{\mathrm{E}}\right)^{-1}. \tag{16}$$

The flux $J(t)$ is provided by the inverse Laplace transform,

$$J(t) = \frac{1}{2\pi i}\int_{0^+-i\infty}^{0^++i\infty}\hat{J}(s)e^{st}\,ds. \tag{17}$$

In what follows, we extend the interpretation of (16) by embedding s in the complex plane, with $\ln s$ being understood to apply in the principal-value sense. The function $\hat{J}(s)$ has

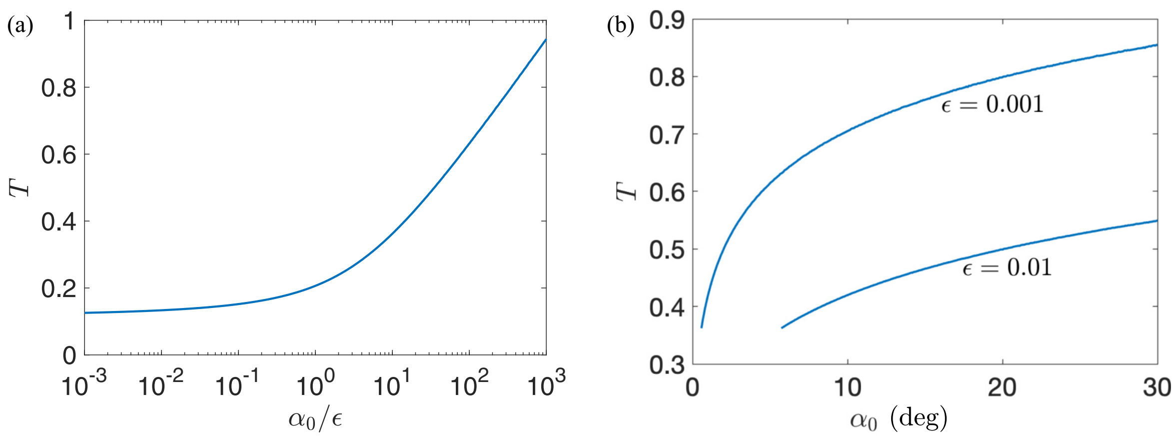

FIG. 3. (a) Universal variation of T with α_0/ϵ. (b) Variation of T with α_0 for the indicated ϵ values.

a branch point at $s = 0$ and a branch cut along the negative real axis. Making use of Cauchy's theorem and Jordan's lemma [22], the integration domain is transformed to two rays that embrace the branch cut, where the integration variable s possesses the respective parametrizations $\lambda e^{\pm i\pi}$, in which λ extends from zero to infinity. Using these parametrizations, we obtain $J(t)$ as the real-valued integral

$$J(t) = \frac{\pi}{2}\int_0^\infty e^{-\lambda t}\left[\left(\frac{1}{2}\ln\frac{16\alpha_0}{\epsilon\lambda} - \gamma_E\right)^2 + \frac{\pi^2}{4}\right]^{-1}\frac{d\lambda}{\lambda}. \tag{18}$$

Since the integrand is of order $\lambda^{-1}(\ln\lambda)^{-2}$ as $\lambda \to 0$, the integral converges at the lower end point. The integral may be readily evaluated for any given value of α_0/ϵ (not necessarily $\gg 1$) using standard numerical quadrature.

With the flux considered a known function of α_0/ϵ, the lifetime T may be obtained for any value of that ratio using the implicit relation (8). The universal variation of T with the single parameter α_0/ϵ is portrayed in Fig. 3(a). While the integral (18) exists for all values of α_0/ϵ, only large values of that parameter are consistent with (6). Illustrative results are depicted in Fig. 3(b), where the variation of T with α_0 (shown here in degrees) is delineated for two representative values of ϵ. In these illustrations we bound α_0 by 10ϵ from below and 30° from above, ensuring that (6) is practically satisfied.

Concluding remarks. Quasisteady diffusive transport in unbounded 2D problems is ill posed due to the incompatibility of the net flux with the need to approach a uniform concentration at infinity. In certain physical problems, this apparent paradox is resolved by incorporating weak advective transport, which enters the dominant balance at large distances [23]. In the present evaporation problem, symmetry arguments would exclude the possibility of regularization by the incorporation of vapor advection. In fact, no need arises to incorporate additional physicochemical mechanisms: the breakdown of the very quasisteady description at large distances gives a hint for resolving the incompatibility. A similar regularization is suitable for 2D diffusion from high-capacity solute beacons [24].

Our scheme avoids the unnecessary use of an artificial boundary at large distances, which in turn introduces an unwarranted dependence upon a nonphysical parameter that cannot be eradicated. Rather, it introduces an essential dependence upon the small parameter of the problem, given here by the ratio of $\Delta c/\Delta\rho$ to the initial contact angle. The dependence of the droplet lifetime upon (the logarithm of) that parameter is a signature of the inherently singular nature of the quasisteady approximation in 2D.

Since the unsteady problem is well posed, one can imagine solving it numerically, with the decay condition replaced by an (approximately equivalent) homogeneous condition at a sufficiently remote boundary. The above discussion clarifies, however, that for the latter equivalence to be indeed valid, the numerical solution must capture the genuinely unsteady process occurring at distances of order $(\alpha_0/\epsilon)^{-1/2}$. This presents a challenge for the integration scheme, which must resolve two disparate length scales. Thus the smaller is ϵ, the greater is the numerical challenge. In the present asymptotic scheme, the approximation level only improves as ϵ diminishes.

With the purpose of illustrating our asymptotic scheme in the simplest possible context, we have assumed thin droplets. The extension to nonthin droplets requires a more detailed analysis in the drop-scale region; the analysis in the remote region remains intact. A different generalization involves the modification of the "constant-radius" model used here, according to which the drop area varies only through the contact angle. Thus one may consider the alternative "constant angle" mode or generalize to more sophisticated modes such as stick–slide [25] and stick–jump [26].

A more ambitious extension involves the analysis of drop arrays [27] where, following methodologies familiar from acoustic interactions [28], the present matching approach is naturally applicable to the limit of well-separated drops.

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