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Evaporation of a thin droplet on a thin substrate with a high thermal resistance

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A mathematical model for the quasisteady evaporation of a thin liquid droplet on a thin substrate that incorporates the dependence of the saturation concentration of vapor at the free surface of the droplet on temperature is used to examine an atypical situation in which the substrate has a high thermal resistance relative to the droplet (i.e., it is highly insulating and/or is thick relative to the droplet). In this situation diffusion of heat through the substrate is the rate-limiting evaporative process and at leading order the local mass flux is spatially uniform, the total evaporation rate is proportional to the surface area of the droplet, and the droplet is uniformly cooled. In particular, the qualitative differences between the predictions of the present model in this situation and those of the widely used “basic” model in which the saturation concentration is independent of temperature are highlighted. © 2009 American Institute of Physics. [DOI: 10.1063/1.3121214]

I. INTRODUCTION

The evaporation of a liquid droplet on a substrate is a fundamental fluid mechanics problem arising in a wide variety of physical contexts ranging from the domestic to the industrial and the geophysical. In recent years new developments in a number of technological applications involving droplet evaporation, notably cooling, desalination, DNA mapping and gene-expression analysis, coating, and patterning have helped to inspire renewed interest in this fascinating problem.

In many physical contexts diffusion of liquid vapor in the atmosphere above the droplet is the rate-limiting evaporative process, and there is now a considerable body of literature concerned with both experimental investigations and theoretical analysis of this situation, including the work of Picknett and Bexon, Bourgès-Monnier and Shanahan, Dee-gan et al., Hu and Larson, Poulard et al., Popov, Sultan et al., Grandas et al., Shahidzadeh-Bonn et al., Guéna et al., Xu and Luo, and Ristenpart et al. Much of the previous theoretical work has focused on this situation, using what we refer to as the “basic” model in which the saturation concentration of vapor at the free surface of the droplet is independent of temperature. Recently David et al. and Dunn et al. conducted a series of physical experiments using a variety of liquids on a variety of substrates and showed that the thermal conductivity of the substrate has a strong influence on the total evaporation rate; moreover, Dunn et al. showed that this behavior can be captured by an improved mathematical model that incorporates the dependence of the saturation concentration of vapor on temperature.

In the present paper we use this improved model to examine an atypical situation in which the substrate has a high thermal resistance relative to the droplet (i.e., it is highly insulating and/or is thick relative to the droplet) so that diffusion of heat through the substrate (rather than diffusion of vapor in the atmosphere) is the rate-limiting evaporative process. In particular, we highlight the qualitative differences between the predictions of the improved model in this situation and those of the basic model.

II. THE MATHEMATICAL MODEL

Adopting the mathematical model proposed by Dunn et al. (who also verified the model by comparison with the experimental results of David et al.) we consider the quasisteady evaporation of a thin pinned axisymmetric sessile droplet with constant radius $R$ of liquid with constant density $\rho$, surface-tension $\sigma$, specific heat capacity $c_p$, and thermal conductivity $k$ on a thin horizontal substrate of constant thickness $h$ with constant density $\rho'$, specific heat capacity $c'_{p}$, and thermal conductivity $k'$. The atmosphere surrounding the droplet and the substrate is assumed to be at constant atmospheric temperature $T_a$ and pressure $p_a$. Referred to cylindrical polar coordinates $(r, \phi, z)$ with origin on the substrate at the center of the droplet and with the $z$ axis perpendicular to the substrate, the shape of the free surface of the droplet at time $t$ is denoted by $z=\eta(r,t)$, the upper surface of the substrate by $z=0$, and the lower surface of the substrate by $z=-h'$, as shown in Fig. 1. The volume of the droplet is denoted by $V=V(t)$, the contact angle at the contact line $r=R$ by $\theta(\theta(t))$, and the initial value of the contact angle at $t=0$ by $\theta_0=\theta(0)$.

Both the droplet and the substrate are assumed to be thin relative to the radius of the droplet, i.e., $\theta_0 \ll 1$ and $h'/R \ll 1$, but no assumption is made about their relative thick-
nnesses, i.e., no assumption is made about the size of $h'/\theta_0 R$. Since both the droplet and the substrate are thin, their temperatures, denoted by $T = T(r, z, t)$ and $T' = T'(r, z, t)$, satisfy $\frac{\partial^2 T}{\partial z^2} = 0$ and $\frac{\partial^2 T}{\partial z^2} = 0$, and the local evaporative mass flux from the droplet, denoted by $J = J(r, z, t)$ (16), satisfies the local energy balance $L J = -k_0 \frac{\partial T}{\partial z}$ on $z = h$ for $r < R$, where $L$ is the latent heat of vaporization. Hence, assuming that both the temperature and the heat flux are continuous between the droplet and the wetted part of the substrate, and that the lower surface of the substrate is at the atmospheric temperature $T_0$, we have simple explicit solutions for the temperature of the droplet and the substrate (in terms of the as yet unknown mass flux $J$), namely

$$T = T_0 - \frac{L J}{k_0} \left( z + \frac{h'}{k_0} \right), \quad T' = T_0 - \frac{L J}{k'} \left( z + h' \right).$$

Assuming that the transport of vapor in the atmosphere is dominated by diffusion (see, for example, Ref. 11), the concentration of vapor in the atmosphere above the droplet and the substrate, denoted by $c = c(r, z, t)$, satisfies Laplace’s equation, $\nabla^2 c = 0$. Since the droplet is thin we may impose the boundary conditions on the free surface of the droplet on $z = 0$ (rather than on $z = h$) and solve Laplace’s equation in the half-space $z > 0$.

At the free surface of the droplet we assume that the atmosphere is saturated with vapor so that $c = c_{s\text{at}}(T)$ on $z = 0$ for $r < R$, where the saturation concentration $c_{s\text{at}} = c_{s\text{at}}(T)$ is assumed to be a linearly increasing function of temperature given by

$$c_{s\text{at}}(T) = c_{s\text{at}}(T_a) + c'_{s\text{at}}(T_a) (T - T_a),$$

in which the dash denotes differentiation with respect to argument (i.e., $c'_{s\text{at}}(T_a) = \frac{dc_{s\text{at}}}{dT}$ evaluated at $T = T_a$). On the dry part of the substrate there is no mass flux, i.e., $\frac{\partial c}{\partial z} = 0$ on $z = 0$ for $r > R$, and far from the droplet the concentration of vapor approaches its ambient value, i.e., $c \rightarrow H c_{s\text{at}}(T_a)$ as $\sqrt{r^2 + z^2} \rightarrow \infty$, where $H$ (0 $\leq H \leq 1$) is the relative saturation of the atmosphere far from the droplet. Once $c$ is known the mass flux from the droplet is given by $J = -D \frac{\partial c}{\partial z}$ on $z = 0$ for $r < R$, where $D$ is the coefficient of diffusion of vapor in the atmosphere, and hence using Eqs. (1) and (2) we find that $c$ satisfies

$$c = c_{s\text{at}}(T_a) + \frac{L D c'_{s\text{at}}(T_a)}{k_0} \left( h + \frac{h'}{k_0} \right) \frac{\partial c}{\partial z} \quad \text{on} \quad z = 0$$

for $r < R$.

A standard result from the theory of gases (see, for example, Ref. 24) is that $D$ is inversely proportional to $p_{\text{sat}}$, i.e., $D = D_{\text{ref}} p_{\text{sat}} / p_{\text{ref}}$, where $D_{\text{ref}}$ and $p_{\text{ref}}$ are reference values of $D$ and $p_{\text{sat}}$, respectively. Note that $p_{\text{sat}}$ enters the model only via this expression for $D$.

To simplify the subsequent presentation we nondimensionalize and scale $r$ with $R$, $z$ in the droplet with $h_0 R$, $z$ in the substrate with $h_0$, $z$ in the atmosphere above the droplet and the substrate with $R$, $h$ with $h_0 R$, $V$ with $h_0 R^2$, $\theta$ with $\theta_0$, $T$ and $T'$ with $T_a$, $c - H c_{s\text{at}}(T_a)$ with $(1 - H) c_{s\text{at}}(T_a)$, $J$ with $D(1 - H) c_{s\text{at}}(T_a) / R$, and $t$ with $\rho_0 \theta_0 R^2 / D(1 - H) c_{s\text{at}}(T_a)$. Hereafter all quantities will be nondimensionalized and scaled appropriately unless stated otherwise.

Assuming that the droplet is sufficiently small that surface-tension effects dominate gravitational effects then it has the simple quasistatic parabolic shape $h = \theta(1 - r^2) / 2$ with volume $V = \pi \theta^2 / 4$, where $\theta(0) = 1$ and $V(0) = \pi / 4$. The total evaporation rate is given by

$$- \frac{dV}{dt} = \pi \int_0^1 r^2 J r dr,$$

where $J$ is given by

$$J = - \frac{\partial c}{\partial z} \quad \text{on} \quad z = 0 \quad \text{for} \quad r < 1.$$

The concentration of vapor in the atmosphere $c$ satisfies $\nabla^2 c = 0$ in $z > 0$ subject to the mixed boundary conditions

$$c = 1 + \Delta C(h + S) \frac{\partial c}{\partial z} \quad \text{on} \quad z = 0 \quad \text{for} \quad r < 1,$$

$$\frac{\partial c}{\partial z} = 0 \quad \text{on} \quad z = 0 \quad \text{for} \quad r > 1,$$

and $c \rightarrow 0$ as $\sqrt{\frac{r^2 + z^2}{\theta_0^2}} \rightarrow \infty$, where

$$\Delta C = \frac{\theta_0 L D c'_{s\text{at}}(T_a)}{k_0} \quad \text{and} \quad S = \frac{kh'}{\theta_0 R k_0^2}$$

are nondimensional measures of the variation of saturation concentration with temperature and of the relative thermal resistance of the droplet and the substrate, respectively. The boundary condition (6), the nondimensional version of Eq. (3), which incorporates the variation of the saturation concentration with temperature given in Eq. (2) and hence couples the problem for the concentration of vapor to that for the temperature, is a key difference between the present model and the basic model used by several previous authors. Once $c$ and hence $J$ are known, the temperature of the droplet and the substrate are given by Eq. (1) to be

$$T = 1 - EJ(z + S), \quad T' = 1 - EJS(z + 1),$$

where
is a nondimensional measure of the evaporative cooling. In particular, Eq. (9) describes the evaporative cooling of the droplet and the substrate below the droplet.

Before investigating the behavior of the model in the situation in which the substrate has a high thermal resistance relative to the droplet (corresponding to the limit \( S \to \infty \)) in Sec. III, in Secs. II A and II B we briefly examine the behavior of the model when \( S = O(1) \) in the two extreme cases in which the saturation concentration is independent of temperature (i.e., \( \Delta C = 0 \)) and in which the saturation concentration is strongly dependent on temperature (i.e., \( \Delta C \to \infty \)).

A. The special case \( \Delta C = 0 \)

In the special case in which the saturation concentration is independent of temperature, corresponding to \( \Delta C = 0 \), the present model reduces to a trivial generalization (namely, to the case in which \( D \) is a known function of \( p_o \)) of the basic model. Specifically, the boundary condition (6) reduces to simply \( c = 1 \) on \( z = 0 \) for \( r < 1 \) so that the problem for the concentration of vapor is decoupled from that for the temperature. The solution for \( c = 0 \) is well known and can be expressed in several equivalent forms including

\[
c = \frac{2}{\pi} \int_0^\infty J_0(\xi r) \sin(\xi R) e^{-\xi z} d\xi,
\]

where \( J_n(\cdot) \) denotes a Bessel function of the first kind of order \( n \), and hence from Eq. (5)

\[
J = \frac{2}{\pi \sqrt{1 - r^2}}.
\]

From Eq. (4)

\[
- \frac{dV}{dt} = 4,
\]

and hence \( V = \pi/4 - 4t \) and \( \theta = 1 - 16t/\pi \), and, in particular, the droplet completely disappears at \( t = \pi/16 \). From Eq. (9)

\[
T = 1 - \frac{2E(z + S)}{\pi \sqrt{1 - r^2}}, \quad T^* = 1 - \frac{2ES(z + 1)}{\pi \sqrt{1 - r^2}}.
\]

In particular, the local mass flux and the temperatures in both the droplet and the substrate are all integrably singular at the edge of the droplet.

B. The limit \( \Delta C \to \infty \)

In the opposite extreme in which the saturation concentration is strongly dependent on temperature, corresponding to the limit \( \Delta C \to \infty \), the boundary condition (6) becomes \( \partial c/\partial z = -2/[\{1 - r^2 + 2S\} \Delta C] + O(1/\Delta C^2) \) on \( z = 0 \) for \( r < 1 \). Although the leading order solution for \( c = O(1/\Delta C) \) cannot readily be expressed in closed form, we can immediately deduce that

\[
J = \frac{2}{(1 - r^2 + 2S)\Delta C} + O\left(\frac{1}{\Delta C^2}\right).
\]

From Eq. (4)

\[
- \frac{dV}{dt} = \frac{2\pi}{\Delta C} \log\left(\frac{1 + 2S}{2S}\right) + O\left(\frac{1}{\Delta C^2}\right),
\]

showing that the first order total evaporation rate is a monotonically decreasing function of \( S \), and hence

\[
V = \frac{\pi}{4} - \frac{2\pi}{\Delta C} \log\left(\frac{1 + 2S}{2S}\right) t + O\left(\frac{1}{\Delta C^2}\right).
\]

and

\[
\theta = 1 - \frac{8}{\Delta C} \log\left(\frac{1 + 2S}{2S}\right) t + O\left(\frac{1}{\Delta C^2}\right).
\]

From Eq. (9)

\[
T = 1 - \frac{2E(z + S)}{(1 - r^2 + 2S)\Delta C} + O\left(\frac{1}{\Delta C^2}\right),
\]

\[
T^* = 1 - \frac{2ES(z + 1)}{(1 - r^2 + 2S)\Delta C} + O\left(\frac{1}{\Delta C^2}\right).
\]

In particular, it is interesting to note from Eq. (19) that the temperature of the free surface of the droplet is given by \( T = 1 - E/\Delta C + O(1/\Delta C^2) \) which is, rather unexpectedly, spatially uniform and constant in time up to \( O(1/\Delta C^2) \).

III. THE LIMIT \( S \to \infty \)

In general, the model described in Sec. II has to be solved numerically, as Dunn et al. \(^{22,23}\) did. However, in the situation in which the substrate has a high thermal resistance relative to the droplet (i.e., it is highly insulating and/or is thick relative to the droplet), corresponding to the limit \( S \to \infty \), we can obtain the asymptotic solution to the problem by seeking an expansion for \( c \) in the form

\[
c = c_0 + \frac{c_1}{\Delta CS} + \frac{c_2}{\Delta C^2 S^2} + O\left(\frac{1}{S^3}\right),
\]

where the factors of \( \Delta C = O(1) \) have been included to simplify the subsequent presentation, with corresponding expansions for all the other dependent variables.

A. Zeroth order

At zeroth order in \( 1/S \) we find immediately that \( c_0 = 0 \), \( J_0 = 0 \), and \( dV_0/dt = 0 \), and hence \( V_0 = \pi/4 \) and \( \theta_0 = 1 \), showing that according to the present model there is, as expected, no evaporation from a droplet on a perfectly thermally resisting substrate.

B. First order

At first order in \( 1/S \) we find immediately that \( J_1 = 1 \) and

\[
- \frac{dV_1}{dt} = 2\pi \int_0^1 J_1 r dr = \pi,
\]

and hence \( V_1 = -\pi t \) and \( \theta_1 = -4t \), and from Eq. (9)
$T_0 = 1 - \frac{E}{\Delta C}$, \hspace{1cm} $T'_0 = 1 - \frac{E(z + 1)}{\Delta C}$. \hspace{1cm} (23)

In other words, the first order mass flux is spatially uniform and constant in time and gives rise to linear decreases in both the volume and the contact angle in time at first order. Moreover, the leading order temperature in both the droplet and the substrate are constant in time, but whereas the temperature in the droplet is spatially uniform (i.e., the droplet is uniformly cooled) that in the substrate below the droplet decreases linearly with $z$ from the atmospheric value of unity at $z = -1$ to the droplet value of $1 - E/\Delta C$ at $z = 0$.

The first order concentration, $c_1 = c_1(r,z)$, satisfies $\nabla^2 c_1 = 0$ subject to

$$\frac{\partial c_1}{\partial z} = \begin{cases} -1 & \text{on } z = 0 \text{ for } r < 1, \\ 0 & \text{on } z = 0 \text{ for } r > 1, \end{cases}$$ \hspace{1cm} (24)

and $c_1 \to 0$ as $\sqrt{r^2 + z^2} \to \infty$. Fortunately, this problem for $c_1$ can be solved explicitly (see, for example, Ref. 25) to yield

$$c_1(r,z) = \int_0^\infty J_0(\xi r) J_1(\xi) e^{-\xi z} \frac{d\xi}{\xi},$$ \hspace{1cm} (25)

where again $J_n(\cdot)$ denotes a Bessel function of the first kind of order $n$. Figure 2 shows contours of $c_1$ in the atmosphere above the droplet and the substrate, and, in particular, illustrates that $c_1 \sim 1/2\sqrt{r^2 + z^2}$ as $\sqrt{r^2 + z^2} \to \infty$. Evaluating $c_1$ on $r = 0$ yields $c_1(0,z) = 1 + t^2 - z$, while evaluating $c_1$ on $z = 0$ yields

\begin{equation}
\begin{aligned}
c_1(r,0) &= \frac{2}{\pi} \times \begin{cases} \mathcal{E}(r) & \text{for } r < 1, \\ \frac{\mathcal{E}(r) - \mathcal{K}(\sqrt{\frac{r^2}{2}})}{r} & \text{for } r > 1, \end{cases} \\
\mathcal{K}(\cdot) \text{ and } \mathcal{E}(\cdot) \text{ are complete elliptic integrals of the first and second kind, respectively, defined by} \\
\mathcal{K}(r) &= \int_0^1 \frac{d\xi}{\sqrt{1 - \xi^2 r^2}}, \\
\mathcal{E}(r) &= \int_0^1 \frac{1 - \xi^2 r^2}{\sqrt{1 - \xi^2}} d\xi. 
\end{aligned}
\end{equation}

(26)

In particular, we find that $c_1(1,0) = 1 - r^2/4 + O(r^4)$ as $r \to 0^+$,

$$c_1(r,0) = \frac{2}{\pi} + \frac{r - 1}{\pi} \left[ 1 + \log \frac{|r - 1|}{8} \right] + O[(r - 1)\log|r - 1|] \text{ as } r \to 1,$n

(27)

showing that $c_1(r,0)$ is continuous with a logarithmic singularity in slope at the edge of the droplet, and

$$c_1(r,0) = \frac{1}{2r} + \frac{1}{16r^2} + O\left(\frac{1}{r^3}\right) \text{ as } r \to \infty. \hspace{1cm} (28)$$

Figure 3 shows a plot of $c_1(r,0)$ as a function of $r$.

C. Second order

At second order in $1/S$ we find that

$$J_2 = -\left(\frac{2E(r) + (1 - r^2)\Delta C}{\pi^2} \right) \hspace{1cm} (<0)$$

(30)

and

$$-\frac{dV_2}{dt} = 2\pi \int_0^1 J_2 r dr = -\left(\frac{8}{3} + \frac{\pi \Delta C}{4}\right) \hspace{1cm} (<0), \hspace{1cm} (31)$$

and hence

$$V_2 = \left(\frac{8}{3} + \frac{\pi \Delta C}{4}\right)t \hspace{1cm} (32)$$

and
\( \theta_2 = \left( \frac{32}{3\pi} + \Delta C \right) t. \) \hspace{1cm} (33)

In particular, from Eq. (30) we find that
\[
J_2 = - \left( \frac{2 + \Delta C}{2} \right) + \left( 1 + 2\Delta C \right) r^2 + O(r^4) \quad \text{as} \quad r \to 0^+,
\]
and
\[
J_2 = - \frac{2}{\pi} \frac{1-r}{2} \log \frac{1-r}{8} + 1 - \pi \Delta C
\]
\[+ O((1-r)^2 \log(1-r)) \quad \text{as} \quad r \to 1^-,
\]
showing that \( J_2 \) remains finite but has a logarithmic singularity in slope at the edge of the droplet. Figure 4 shows a plot of \( J_2 \) as a function of \( r \) for a range of values of \( \Delta C \). From Eq. (9)
\[
T_1 = -E \left[ z - \frac{2E(r)}{\pi \Delta C} + \frac{(1-r^2)}{2} \right]
\]
and
\[
T_1 = E(z+1) \left[ \frac{2E(r)}{\pi \Delta C} + \frac{(1-r^2)}{2} \right].
\]

In other words, the second order mass flux is negative and spatially nonuniform but constant in time and gives rise to linear increases in both the volume and the contact angle in time at second order. The second order concentration, \( c_2 = c_2(r,z) \), satisfies \( \nabla^2 c_2 = 0 \) subject to
\[
\frac{\partial c_2}{\partial z} = \left\{ \begin{array}{ll}
2E(r) & \text{on } z = 0 \quad \text{for} \quad r < 1, \\
\frac{2E(r)}{\pi} & \text{on } z = 0 \quad \text{for} \quad r > 1,
\end{array} \right.
\]
and \( c_2 \to 0 \) as \( \sqrt{r^2 + z^2} \to \infty \). This problem for \( c_2 \) cannot readily be solved in closed form, but fortunately, as we have already seen, we do not need to determine \( c_2 \) in order to obtain \( J \) and \( dV/dt \) to \( O(1/S^2) \) and \( T \) and \( T' \) to \( O(1/S) \).

**D. Range of validity of the asymptotic solution**

In order to determine the range of validity of the present asymptotic solution Fig. 5 shows a plot of \( -dV/dt \) as a function of \( S \) for a range of values of \( \Delta C \) comparing the present asymptotic solution and the exact numerical solutions calculated using a finite-element method implemented using the MATLAB-based numerical analysis package COMSOL MULTIPHYSICS (formerly FEMLAB) as described by Dunn et al.\(^{(22,23)}\)

In particular, Fig. 5 confirms that the present asymptotic solution is indeed in good agreement with the exact solution provided that \( S \) is sufficiently large, and that, as expected, what precisely “sufficiently large” means depends on the value of \( \Delta C \).

**IV. DISCUSSION**

While the present nondimensional presentation is mathematically very convenient it obscures the way the variables depend on the original physical quantities, and so it is enlightening to write the asymptotic solution described in Sec. III in dimensional terms as follows:
\[
c = H \frac{c_{sat}(T_d) + k^2 R(1-H)c_{sat}'(T_d)}{L h^4 c_{sat}'(T_d)} \int_0^\infty \frac{J_0(\xi r)J_1(\xi R)e^{-\xi}}{\xi} d\xi
\]
\[+ O\left(\frac{\theta_0 R k^2}{kh^4}\right)^2,
\]
\[
J = \frac{k^2(1-H)c_{sat}(T_d)}{L h^4 c_{sat}'} \left[ 1 - \left( \frac{2kE(r/R)}{\pi \theta_0 L D c_{sat}'} \right) \right] + O\left(\frac{\theta_0 R k^2}{kh^4}\right)^3,
\]
\[
T = T_a - \frac{(1-H)c_{sat}(T_d)}{c_{sat}'(T_a)} \left[ 1 + \left( \frac{z}{\theta_0 R} - \frac{2kE(r/R)}{\pi \theta_0 L D c_{sat}'} \right) \right] + O\left(\frac{\theta_0 R k^2}{kh^4}\right)^2,
\]
\[
T' = T_a - \frac{(1-H)c_{sat}(T_d)}{c_{sat}'(T_a)} \left[ 1 + \left( \frac{z}{h^4} + 1 \right) - \left( \frac{2kE(r/R)}{\pi \theta_0 L D c_{sat}'} \right) \right] + O\left(\frac{\theta_0 R k^2}{kh^4}\right)^2,
\]

**FIG. 4.** Plot of \( J_2 \) as a function of \( r \) for \( \Delta C=0.1, 1, \) and 10.

**FIG. 5.** Plot of \( -dV/dt \) as a function of \( S \) for \( \Delta C=0.1, 1, \) and 10 comparing the present asymptotic solution and the exact numerical solutions.
As with any mathematical model, there are a number of conditions restricting the validity of the present analysis. For the mathematical model of Dunn et al. used in the present work to hold we require that fluid inertia is negligible, i.e.,
\[ \frac{\theta_0^2 \rho U R}{\mu} \ll 1, \]
that thermal advection is negligible, i.e.,
\[ \frac{\theta_0^2 \rho c \rho U R}{k} \ll 1, \]
where \( U \) is a characteristic radial velocity, that the temperature in the droplet is quasisteady, i.e.,
\[ \frac{\rho c_p (\theta_0 R)^2}{k T} \ll 1, \]
that the diffusion in the atmosphere is quasisteady, i.e.,
\[ \frac{R^2}{D T} \ll 1, \]
where \( T \) is the characteristic lifetime of the droplet, that gravity effects are negligible in the droplet, i.e.,
\[ \frac{\rho g R^2}{\sigma} \ll 1, \]
and that the thermal conductivities of both the fluid and the substrate are greater than that of the surrounding air, denoted by \( k_{\text{air}} \), i.e.,
\[ k, k^i \gg k_{\text{air}}. \]
In addition, for the simplified version of the model used in the present work to hold we require that both the droplet and the substrate are thin (i.e., that the thicknesses of both the droplet and the substrate are small relative to the radius of the droplet), i.e.,
\[ \theta_0 \ll 1 \quad \text{and} \quad \frac{h^i}{R} \ll 1. \]
Finally, for the large-\( S \) asymptotic analysis described in Sec. III to hold we require that
\[ S = \frac{h^i}{\theta_0 R k^i} \gg 1 \quad \text{with} \quad \Delta C = \frac{\theta_0 \rho L D c'_s(T_a)}{k} = O(1). \]
with typical parameter values for polypropylene, namely \( \rho = 998 \text{ kg m}^{-3} \), \( \mu = 9.62 \times 10^{-4} \text{ kg m}^{-1} \text{s}^{-1} \), \( c_p = 4.18 \times 10^3 \text{ m}^2 \text{s}^{-2} \text{K}^{-1} \), \( k = 0.604 \text{ kg m s}^{-1} \text{K}^{-1} \), \( \sigma = 7.25 \times 10^{-2} \text{ kg s}^{-2} \text{K}^{-1} \), \( c_{\text{sat}}(T_a) = 1.94 \times 10^{-2} \text{ kg m}^{-3} \), \( c'_{\text{sat}}(T_a) = 1.11 \times 10^{-3} \text{ kg m}^{-3} \text{K}^{-1} \), and \( D = 2.44 \times 10^{-4} \text{ m}^2 \text{s}^{-1} \), together with typical parameter values for polypropylene, namely \( \rho' = 910 \text{ kg m}^{-3} \), \( c'_p = 1.9 \times 10^3 \text{ m}^2 \text{s}^{-2} \text{K}^{-1} \), \( k' = 0.12 \text{ kg m}^{-3} \text{s}^{-1} \), the characteristic lifetime of the droplet in the large-\( S \) asymptotic limit is

\[
T = \frac{\rho \theta_d R^2}{D(1-H)c_{\text{sat}}(T_a)} S \Delta c = \frac{\rho L h^4 c_{\text{sat}}(T_a)}{k'(1-H)c_{\text{sat}}(T_a)} \approx 10 \text{ s},
\]

and hence a characteristic radial velocity is \( U = R/T = 5 \times 10^{-5} \text{ m s}^{-1} \). Using these parameter values the left hand sides of conditions (48)–(53) are small, specifically \( 3 \times 10^{-4}, 2 \times 10^{-3}, 2 \times 10^{-3}, 0.01, 1 \times 10^{-4}, \) and 0.03, respectively. Furthermore, condition (54) holds because the conductivities of both the droplet and the substrate are significantly greater than that of air (typically \( 0.02 \text{ kg m}^{-3} \text{K}^{-1} \)). In addition, condition (55) holds because both \( \theta_t = 0.1 \) and \( h/R = 0.2 \) are small, while Eq. (56) yields \( S \approx 10 \) and \( \Delta c = 0.1 \), which Fig. 5 indicates is just in the asymptotic regime. Clearly it is also possible to imagine other situations with somewhat larger values of \( S \), but the foregoing suggests that the present asymptotic analysis is relevant to a physically realistic situation that could be realized in the laboratory using the approach and techniques used by, for example, David et al.\(^{21}\)

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