

Seminar 3: Mathematical Aspects of Droplet Evaporation

Wednesday: November 11, 2020 9:45 → 11:15

Speaker: David Pitchard

Discussing: mathematical physics, analysis of PDEs, classical analysis and ODEs, fluid dynamics

* Consider a droplet of water how long will it last?
History:

Harry W. Morse (1910): experiments show a droplet evaporates at a rate proportional to its radius.
Irving Langmuir (1918): presents first analysis of the evaporation of an isolated droplet.

Some Current Applications

- Cooling and wetting.
 - agricultural irrigation
 - spray cooling and air conditioning.
- Printing and manufacture
 - ink-jet printing.
 - printed circuit boards.
- Biomedical applications
 - spray decontamination
 - DNA micro-array deposition
- Applications to the culture of mathematics
 - coffee stains.

History: James Clerk Maxwell develops the Kinetic theory of gases c. 1860 including the concept of molecular diffusion.

Physics:

Transfer of heat and mass

- Simplest case: diffusive transport only
- Additional effects: convection, imbibition

Fluid Dynamics

- Simplest case: no flow, droplet shape controlled by surface tension / pressure balance
- Additional effects: internal flow; Marangoni forces
- Contact-line dynamics: an open problem

Physics: evaporative flux models

Diffusion-limited [e.g. Picknett & Bexon 1977; Popov 2005]

- Vapour concentration is saturated at the interface:
$$c = c_{\text{sat}}(T)$$
- Vapour flux from the interface is purely diffusive
$$J = -n \cdot (D \nabla c)$$
- Temperature is continuous and energy balance satisfies
$$LJ = n \cdot (k^a \nabla T^a - k^v T)$$

Key assumption: local thermodynamic equilibrium

One-Sided [e.g. Ajaev et al. 2001]

- Vapour flux from the interface is driven by a vapour pressure jump.

$$J = \alpha P_v \sqrt{\frac{RT}{2\pi}} \left(\frac{P_v^{\text{sat}}}{P_v} - 1 \right)$$

(Hertz-Knudsen - Langmuir formula)

- Atmospheric vapour concentration is irrelevant.
- Temperature may be discontinuous.

Key assumption: local thermodynamic non-equilibrium

Possibly appropriate for very rapid evaporation... but always beware non-equilibrium thermodynamics!

Physics: Regimes

* Key dimensionless regime parameters:

→ Eötvös - Bond number: $B_0 = \frac{R^2 \rho g}{\sigma}$
compares gravitational to capillary forces.

→ Capillary number: $Ca = \frac{\mu U}{\sigma}$
compares viscous to capillary forces

→ Péclet number: $Pe = \frac{RU}{D}$
compares advective to diffusive transport.

→ Fourier numbers: $F_0 = \frac{\pi D}{R^2}$
compare evaporative to diffusive timescales.

If the evaporation is diffusion-limited then $U = R/T$ and $F_0 = 1/Pe$

* Typical regime for "every day" evaporation processes:

→ Small Eötvös - Bond number: $B_0 = \frac{R^2 \rho g}{\sigma} \ll 1$
constant interface curvature

→ Small capillary number: $Ca = \frac{\mu U}{\sigma} \ll 1$
neglect internal flow

→ Small Péclet numbers: $Pe = \frac{RU}{D} \ll 1$
neglect advective transport

→ Large Fourier numbers: $F_0 = \frac{\pi D}{R^2} \gg 1$
quasi-steady evaporation

* Thermally uncoupled problems: isolated droplets
Consider an isolated spherical droplet in a spherical atmosphere in 3D.

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dc}{dr} \right) = 0 \quad \left\{ \begin{array}{l} c = c_{sat} \text{ on } r = R \\ c = c_{\infty} \text{ on } r = R_{\infty} \end{array} \right.$$

General Solution: $c(r) = A + \frac{B}{r}$ where $B = \frac{(c_{sat} - c_{\infty}) R R_{\infty}}{R_{\infty} - R}$

Hence the mass flux from the droplet surface is $-D \frac{dc}{dr} = \frac{BD}{R^2}$, and the integrated mass flux over the surface is:

$$\frac{4\pi D (c_{\text{sat}} - c_{\infty}) R R_{\infty}}{R_{\infty} - R} \rightarrow 4\pi D (c_{\text{sat}} - c_{\infty}) R \text{ as } R_{\infty} \rightarrow \infty$$

This is Langmuir's (1918) result.

2D * Now consider an isolated circular droplet in a circular atmosphere in 2D.

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dc}{dr} \right) = 0, \quad \begin{cases} c = c_{\text{sat}} \text{ on } R = r \\ c = c_{\infty} \text{ on } r = R_{\infty} \end{cases}$$

General Solution:

$$c(r) = A + B \ln(r) \text{ where } B = \frac{(c_{\text{sat}} - c_{\infty})}{\ln(R/R_{\infty})}$$

Hence the mass flux from the droplet surface is $-D \frac{dc}{dr} = \frac{BD}{R}$, and the integrated mass flux over the surface is:

$$\frac{2\pi D (c_{\text{sat}} - c_{\infty})}{\ln(R/R_{\infty})} \text{ which is unbounded as } R_{\infty} \rightarrow \infty$$

as we cannot take the boundary "at infinity" in 2D

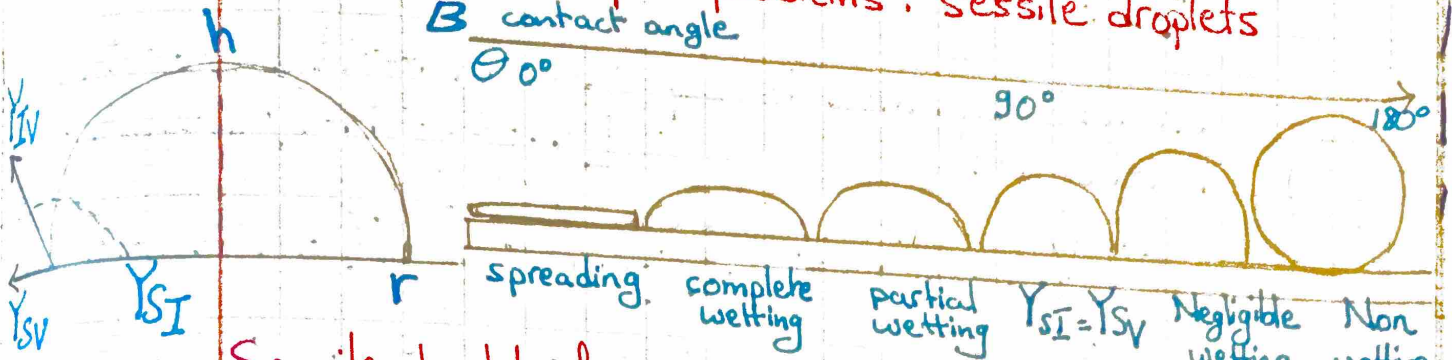
Thermally uncoupled problems: sessile droplets

θ contact angle

0°

90°

180°



Sessile droplets for various contact angles [Garcia-Cordero & Fan 2017]

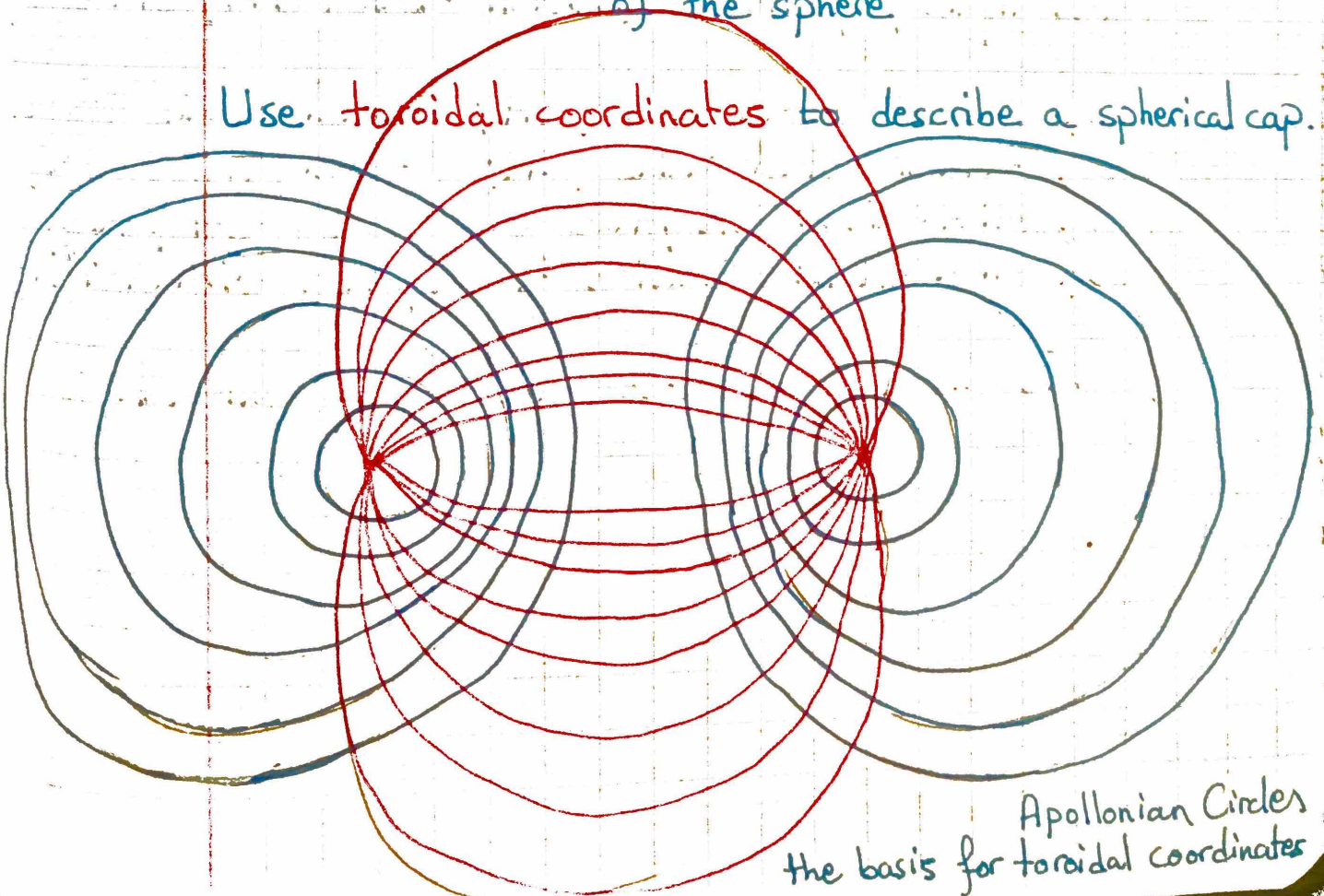
Small Eötvös-Bond number: spherical cap

$$z = h = \pm \sqrt{\frac{R^2}{\sin^2 \theta} - r^2} - R \cot(\theta)$$

→ Contact angle $\theta(t)$ is controlled by local dynamics and surface roughness.

→ Contact radius: $R(t) = R \sin(\theta)$ where R is radius of the sphere

Use toroidal coordinates to describe a spherical cap.



Apollonian Circles
the basis for toroidal coordinates

Use toroidal coordinates to describe a spherical cap.

Laplace's equation is separable in toroidal coordinates leading to: [Lebedev 1965; Deegan et al. 2000]

$$J = \frac{D(C_{\text{sat}} - C_{\infty})}{R} \left[\frac{1}{2} \sin(\theta) + \sqrt{2} (\cosh(\alpha) + \cos(\theta))^{3/2} \right]$$
$$\times \int_0^{\infty} \frac{T \cosh(\theta T)}{\cosh(\pi T)} \tanh [T(\pi - \theta)] P_{-\frac{1}{2} + ir}(\cos(\alpha)) dT$$

$$\text{where } \cosh(\alpha) = \frac{r^2 \cos(\theta) \pm R \sqrt{R^2 - r^2 \sin^2 \theta}}{R^2 - r^2}$$

* Non-uniform evaporative flux leads to internal flow. Consequence: the coffee-stain effect. [Deegan et al. 2000]

The evaporative flux determines the evolution of the droplet's volume. What about its shape?

The mode of evaporation is controlled by substrate and liquid properties [Picknett & Bexon 1977; Stauber 2015]

- constant contact angle (CA; contact radius evolves)
- constant contact radius (CR; contact angle evolves)
- stick-slide: CR phase followed by CA phase.
- stick-jump: succession of CR phases with short "jumps"

The CA and CR modes are usually external.

Thermally coupled problems: isolated droplets.

3D * Consider an isolated spherical droplet in a spherical atmosphere in 3D

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dc}{dr} \right) = 0 \quad \left\{ \begin{array}{l} c = c_{\text{sat}}(T_0) \text{ on } r=R \\ c \rightarrow c_{\infty} \text{ as } r \rightarrow \infty \end{array} \right.$$

and

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT^a}{dr} \right) = 0 \quad \left\{ \begin{array}{l} T^a = T_0 \text{ on } r=R \\ T^a \rightarrow T_{\infty} \text{ as } r \rightarrow \infty \end{array} \right.$$

- Droplet temperature T_0 : constant due to symmetry
- Air temperature: $T^a(r)$

$$\text{Coupling: } k^a \frac{dT^a}{dr} = -LD \frac{dc}{dr} \text{ at } r=R$$

Solution:

$$c = c_{\infty} - \frac{k^a}{LD} (T_0 - T_{\infty}) \frac{R}{r},$$

$$T^a = T_{\infty} + (T_0 - T_{\infty}) \frac{R}{r} \quad \text{subject to}$$

$$c_{\text{sat}}(T_0) - c_{\infty} = \frac{k^a}{LD} (T_{\infty} - T_0)$$

In general $c_{\text{sat}}(T_0)$ is an increasing function of T_0

- Evaporation cools the droplet via latent heat.
- In turn this reduces the concentration gradient
— negative feedback reduces evaporation rate.

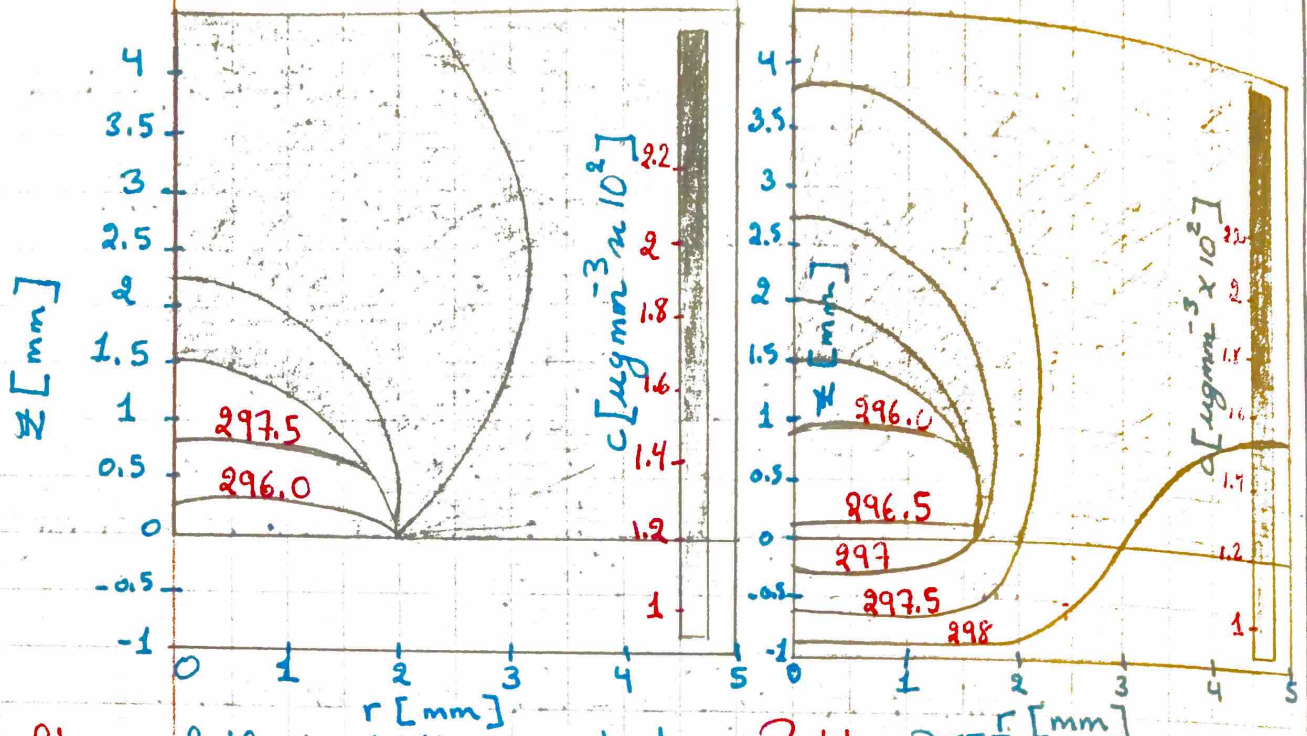
Thermally
Coupled
Problems
Sessile
Droplets.

* Geometrically complex problems (currently) require numerical methods (e.g. finite elements)

Challenges for numerical analysis: [Schofield 2020]

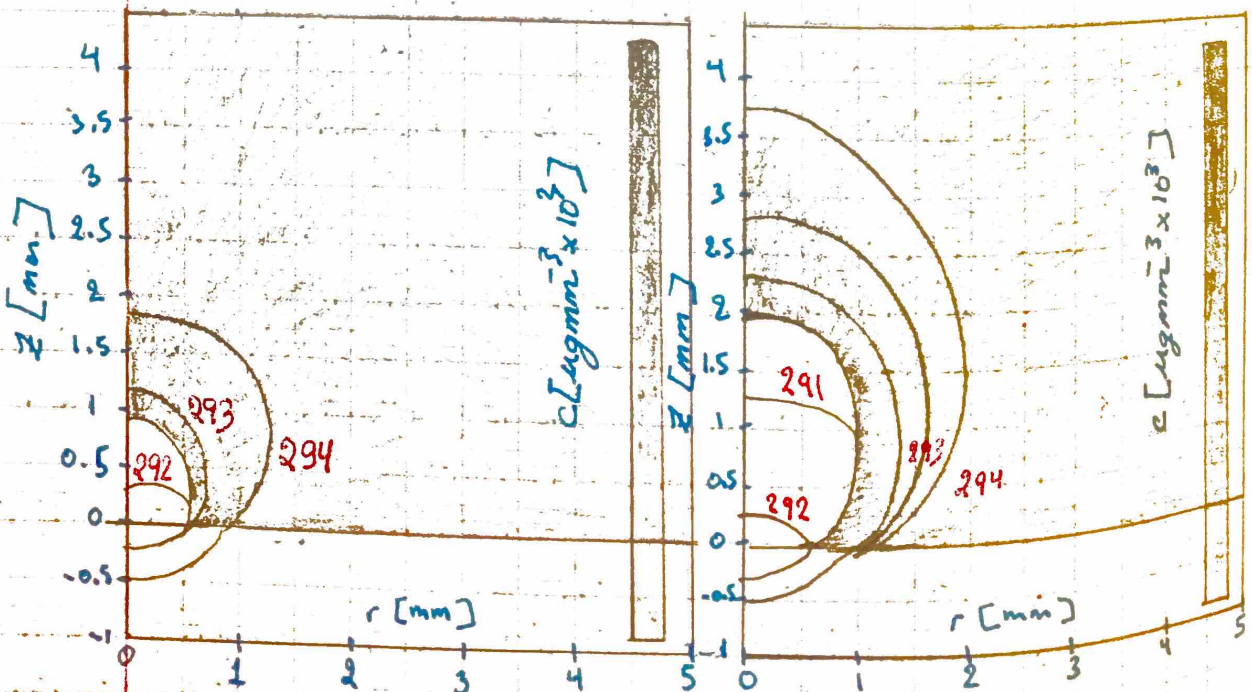
- Strongly coupled problem
- Efficient integration require smart/adaptive meshing.
- Slender grid elements near contact line for hydrophobic droplets ($\theta \rightarrow \pi$)
- Time-stepping and domain evolution.

Thermally Coupled Problems: Sessile Droplets



Left: perfectly conducting substrate : Right: PTFE substrate

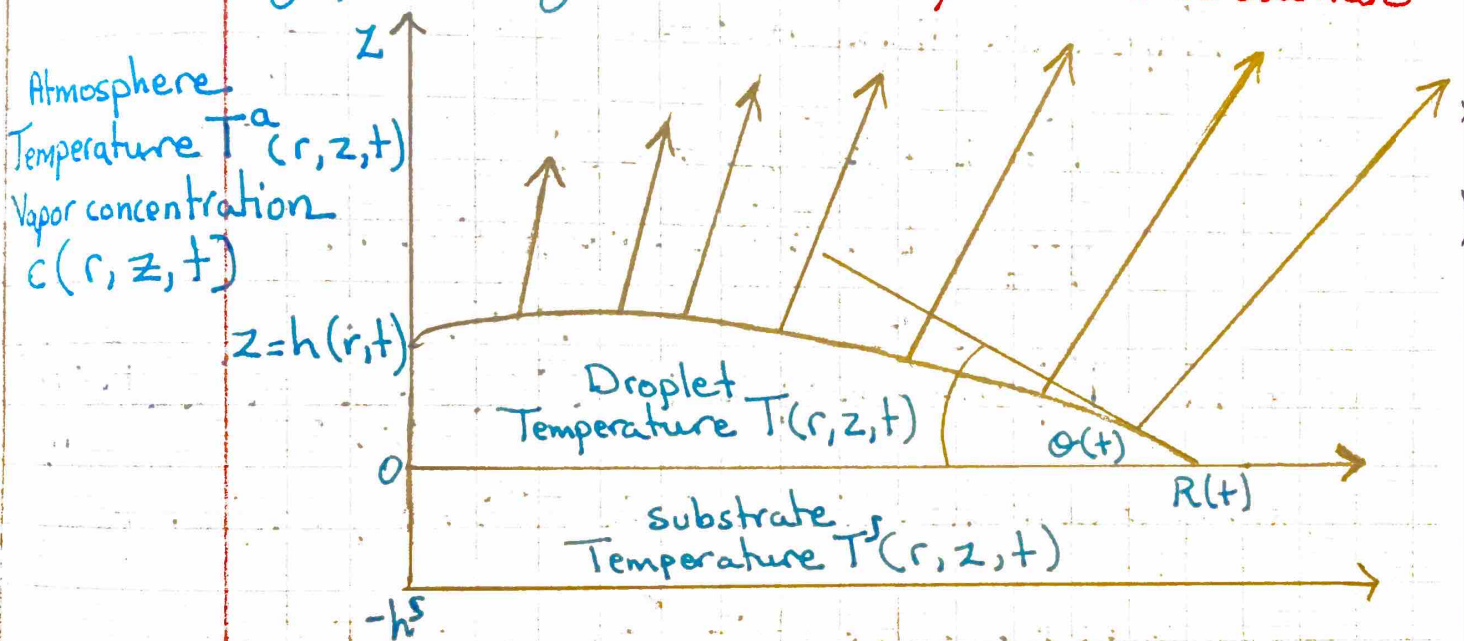
- Evaporative cooling (latent heat) reduces C_{sat} on droplet surface - negative feedback as this reduces vapor flux.
- Thermal anchoring via substrate reduces cooling.



→ Same contact area but different contact angles. At higher contact angles, direct thermal communication is reduced; however, the role of the atmosphere becomes important.

We can thus calculate **lifetimes** in constant-radius mode and constant angle mode.

- Solid lines: thermally uncoupled problem. Coupling extends droplet lifetimes.
- Different symbols: different substrates.
- Lifetimes (almost) converge as $\theta \rightarrow \pi$.
- ⇒ **Thermally Coupled Problems: thin droplets** ←
- * To explore thermal effects we consider a limiting asymptotic regime: a thin droplet on a thin substrate



Thin droplet: $\frac{h}{R} \ll 1$.

- Can approximate the droplet profile as a parabola

$$z = h(r, t) = \theta(t) \frac{R^2(t) - r^2}{2R(t)}; \text{ volume } V(t) \Rightarrow$$

$$V(t) = \frac{\pi}{4} \theta(t) R^3(t)$$

- Heat equation within droplet reduces to $\frac{d^2 T}{dz^2} = 0$
- Thin substrate: $\frac{h^s}{R} \ll 1$

- Heat equation within substrate reduces to $\frac{d^2 T^s}{dz^2} = 0$

Rescale using:

- horizontal lengthscale $R(0)$
- initial angle $\theta(0)$
- timescale $\frac{\rho \theta(0) R^2(0)}{D(1-H)c_{\text{sat}}(T_{\infty})}$; [Stauber et al. 2014]
- vertical lengthscales $R(0), h^s, \theta(0)R(0)$ (droplet);
- and the natural scales for c and T .

* Temperature fields become

$$T = 1 - EJ(z + S);$$

$$T^s = \begin{cases} 1 - EJS(z + D), & r < R \\ 1 & r > R \end{cases}$$

* Then T^a problem decouples if $k^a \ll \frac{k}{\theta(0)}$, $k^a \ll \frac{R(0)k^s}{h^s}$

* The concentration field satisfies $\nabla_c^2 = 0$, subject to

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

$$\frac{dc}{dz} = 0 \quad \text{on } z < 0, z > R.$$

$$c \rightarrow 0 \quad \text{as } r^2 + z^2 \rightarrow \infty$$

* The evaporation rate is given by

$$\frac{dV}{dt} = 2\pi \int_0^R r J(r, t) dr, \quad \text{where } J = - \left. \frac{dc}{dz} \right|_{z=0}$$

* Dimensionless parameters

$$\Delta C = \frac{\theta(0) L D c'_{\text{sat}}(T_{\infty})}{K} \quad (\text{controls } c_{\text{sat}} \text{ feedback})$$

$$S = \frac{kh^s}{\theta(0) R(0) K^s} \quad (\text{substrate thermal resistance})$$

$$E = \frac{\theta(0) L D (1-H) c_{\text{sat}}(T_{\infty})}{K T_{\infty}} \quad (\text{evaporative cooling})$$

We will consider the regime $S \gg 1$, $\Delta C = O(1)$, $E = O(1)$

In the regime $S \gg 1$, $\Delta C = O(1)$, $E = O(1)$,

$$c = 1 + \Delta C (h+S) \frac{dc}{dz}$$

forces the rescaling.

$$c = \frac{\tilde{c}}{S}, \quad \tilde{J} = \frac{\hat{J}}{S}, \quad \text{and} \quad t = S \hat{t}$$

We end up with,

$$\hat{J} = \frac{1}{\Delta C} + O\left(\frac{1}{S}\right), \quad \frac{d}{d\hat{t}} (\theta R^3) = -\frac{4R^2}{\Delta C} + O\left(\frac{1}{S}\right)$$

It is instructive to compare the timescales for evaporation

⇔ Thermally uncoupled: [Stauber et. al. 2014]

$$T = \frac{P \theta(0) R^2(0)}{D(1-H) c_{\text{sat}}(T_{\infty})}$$

This represents diffusive transport over a distance $O(R)$.

⇔ Strongly thermally coupled [Stauber et. al. 2014]

$$S \Delta C T = \frac{P \theta(0) R(0) h^s L c'_{\text{sat}}(T_{\infty})}{(1-H) c_{\text{sat}}(T_{\infty}) K^s}$$

This represents the ability of the substrate to reduce the negative cooling - evaporation feedback.

Multiple Droplets: a 2D problem

Consider a "toy" isothermal problem with a single flat droplet

$$\nabla^2 c = 0 \text{ in } y > 0, \quad x^2 + y^2 \leq \gamma^2$$
$$c(x, 0) = 1 \text{ for } |x| < R, \quad \frac{dc}{dy}(x, 0) = 0 \text{ for } |x| > R$$

with the far-field BC.

- $c = 0$ on $y > 0, \quad x^2 + y^2 = \gamma^2$
- A 2D problem: can't impose far-field BC at infinity
 - No closed-form solution as posed
 - We relax the shape of the boundary and apply conformal mapping. [Strofield et al 2020]

The function $\phi(u, v) = 1 - \frac{v}{S} = 1 - \frac{\text{Im}(w)}{S}$ satisfies

$$\phi(u, 0) = 1, \quad \frac{d\phi}{du}(-1, v) = 0 = \frac{d\phi}{du}(1, v), \quad \phi(u, S) = 0$$

and hence the function

$$c(x, y) = 1 - \frac{\text{Im}(g^{-1}(z))}{S} = 1 - \frac{1}{\text{arcsinh}(\Psi/R)} \text{Im} \left[\text{arccosh} \left(\frac{z}{R} \right) \right]$$

satisfies our problem... except the "far-field" boundary is now

$$z = \sqrt{\Psi^2 + R^2} \cos(s) + i \Psi \sin(s)$$

Instead of

$$z = \gamma \cos(s) + i \gamma \sin(s).$$

However, as $\Psi \rightarrow \infty$ these agree up to $O(R^{-1})$ when $\gamma = \Psi$

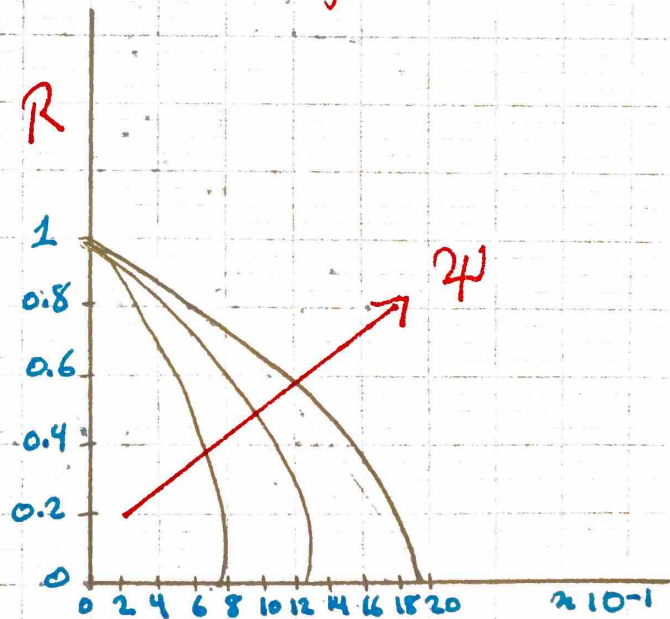
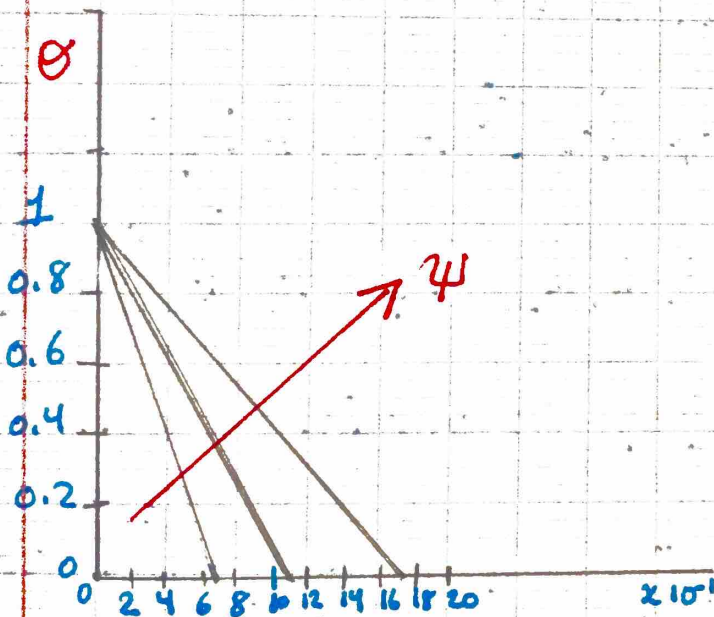
Equipped with the (asymptotic) solution

$$c(x, y) = 1 - \frac{\text{Im}(g^{-1}(z))}{S} = 1 - \frac{1}{\text{arcsinh}(\psi/R)} \text{Im} \left[\arccos\left(\frac{-z}{R}\right) \right]$$

we can calculate the flux.

$$J = -\frac{dc}{dy}(x, 0) = \frac{1}{\text{arcsinh}(\psi/R)} \frac{1}{\sqrt{R^2 - x^2}} \quad \text{for } |x| < R.$$

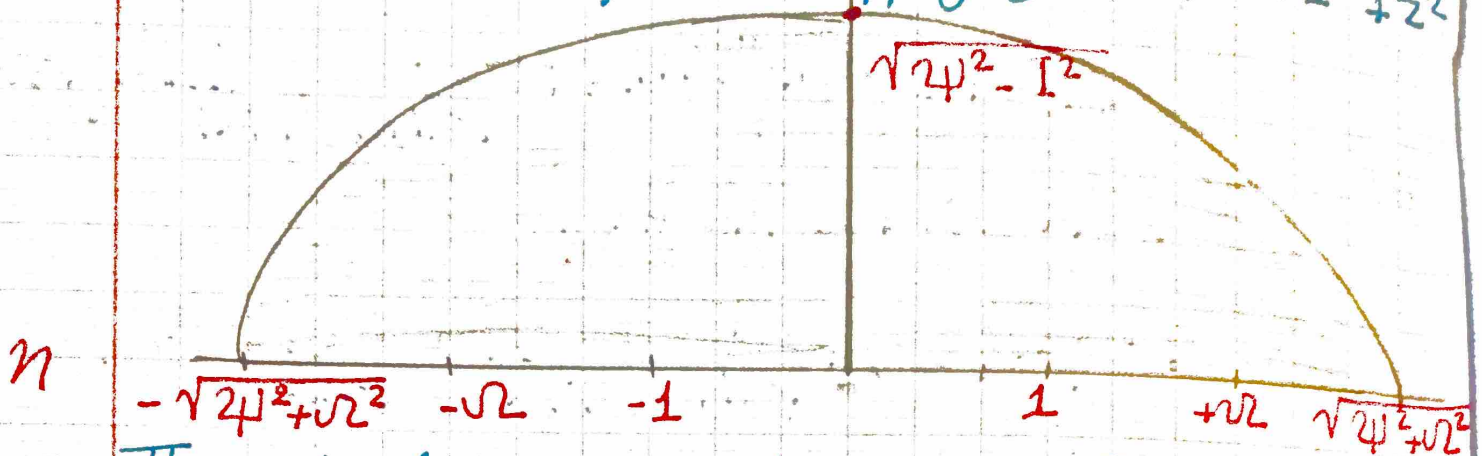
and thus the droplet evolution and lifetimes.



and thus the droplet evolution and lifetimes e.g.

$$t_{CR} = \frac{2}{3\pi} \text{arcsinh}(\psi), \quad t_{CA} = t_{CR} + \frac{2\psi}{3\pi} (\sqrt{\psi^2 + 1} - \psi)$$

Now consider the further mapping $S = \Gamma(z) = \sqrt{I^2 + z^2}$



The rectangle $-1 \leq u \leq 1$, $0 \leq v \leq S$ maps to the quasi-ellipse bounded by

$$S = \left[I^2 + \sqrt{\psi^2 + \omega^2 - I^2} \cos(s) + i \psi \sin(s) \right]^{\frac{1}{2}}$$

The droplet $z \in [-1, 1]$ maps to $\pm S \in [I, \Omega]$ $0 \leq s \leq \pi$

Setting $S = \eta + i\varepsilon$, we obtain

$$c(\eta, \varepsilon) = 1 - \frac{1}{\operatorname{arcsinh}(\psi / \sqrt{\omega^2 - I^2})} \operatorname{Im} \left[\arccos \left(\frac{\sqrt{S^2 - I^2}}{\sqrt{\omega^2 - I^2}} \right) \right]$$

We can now explore various modes of interaction e.g.

- both contact lines pinned (shortest lifetime)
- centers of both drops pinned
- outer contact lines pinned
- inner contact lines pinned (longest lifetime)

Multiple Droplets: a 3D problem

What about multiple droplets in 3D?

One approach

[Wray, Duffy & Wilson 2020]

- Treat N droplets as flat circles in the plane.
- Use integral transforms [Fabricant 1985] to combine fluxes.

$$J_k = J_0 \left[1 - \frac{1}{2\pi} \sum_{n=1, n \neq k}^N \iint_{S_n} \frac{\sqrt{p'^2 - a^2} J_n(p', \phi') p' dp' d\phi'}{p^2 + p'^2 - 2pp' \cos(\phi - \phi')} \right]$$

- Asymptotic expansion for widely separated droplets.

* Some active areas of research.

Marangoni effects: induced internal flow and transport contact-line behavior.

Evaporation of multi-component droplets e.g. alcohol and water

Non-circular droplets: Typically on patterned substrate