Coarsening of dewetting thin films subject to gravity

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Introduction

Uniform fluid films on hydrophobic solid substrates can "dewet" due to intermolecular forces to form drops. These drops interact over long times through the adsorbed ultra-thin film (UTF) to coalesce into fewer but larger drops, until only one drop remains at equilibrium. We call the disappearance of drops coarsening.

We model coarsening using the lubrication equation

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(h^3 \frac{\partial p}{\partial x}\right)$$

where the pressure $p(x,t)$ has three contributing effects,

$$p = \underbrace{-\frac{\partial^2 h}{\partial x^2}}_{\text{Surface Tension}} + \underbrace{\frac{\delta^2}{h^3}\left(1-\frac{\delta}{h}\right)}_{\text{Van der Waals}} + \underbrace{\alpha h}_{\text{Gravity}}.$$

δ — Ratio of average UTF height to average drop height height

α — Ratio of gravitational to van der Waals forces

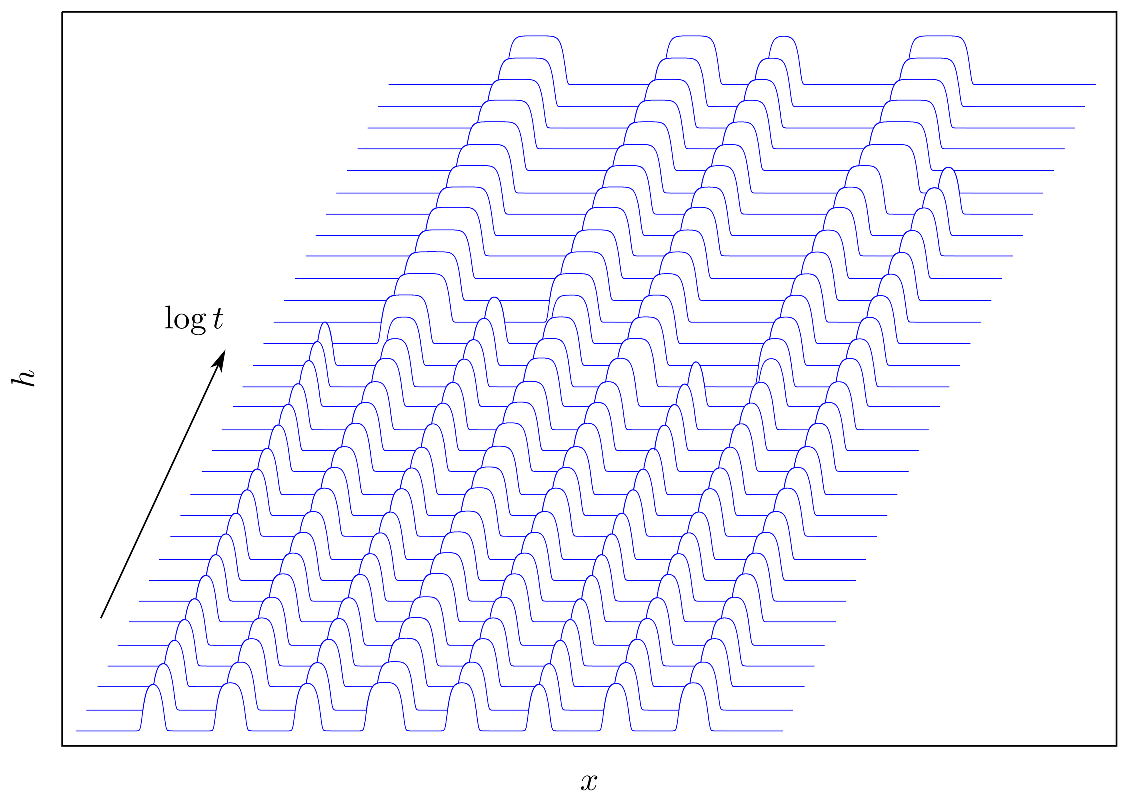


Figure 1: We solve above PDE numerically starting with an array of drops and observe drops moving and exchanging mass. Eventually some disappear, having lost all of their mass to their neighbors.

Single-drop solutions

Steady-state droplet solutions on $-\infty < x < \infty$ occur when $p = P$, a constant,

$$\frac{d^2h}{dx^2} = \Pi(h) + \alpha h - P.$$

This ODE has three fixed points in the phase plane:

- h_m — The height of the surrounding wetting layer, $\mathcal{O}(\delta)$, and a saddle point
- h_c — An ellptic center point
- h_α — A saddle point that limits the maximum drop height

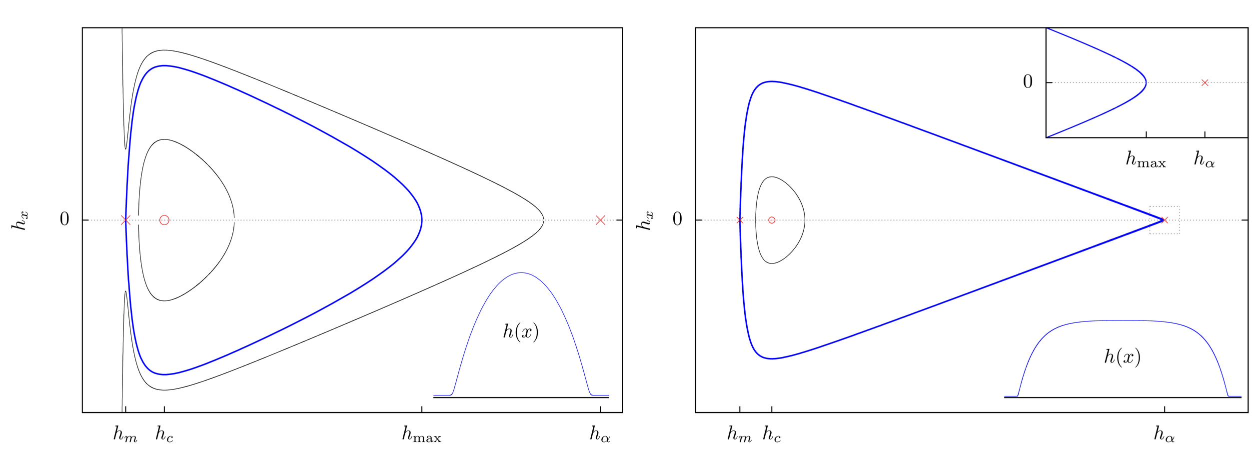


Figure 2: Phase plane showing a drop solution (blue curve) is homoclinic to h_m. Left: Large P leads to parabolic drops with h_α far away. Right: Small P gives mesa-shaped drops with h_{max} constrained by h_α.

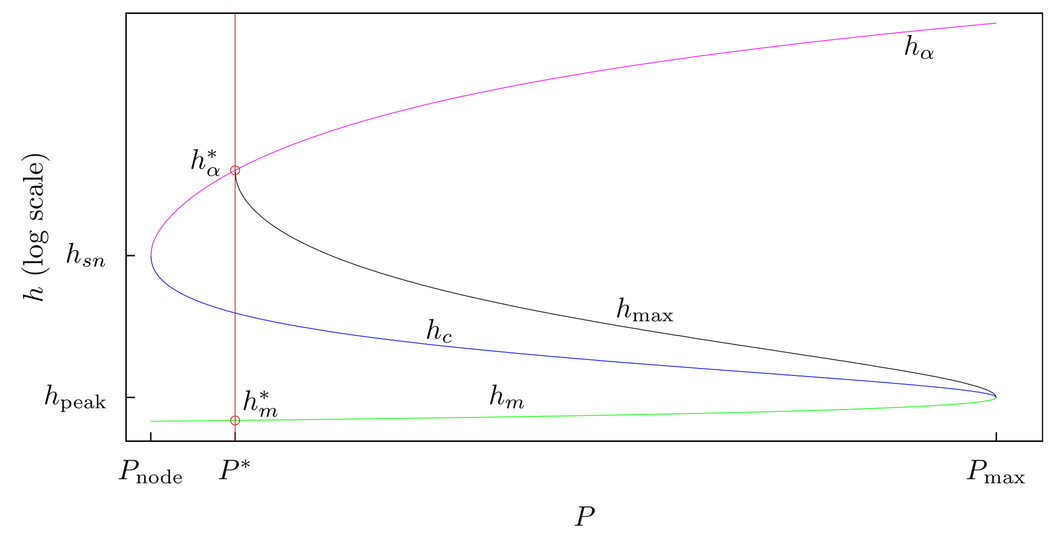


Figure 3: Bifurcation diagram showing how $\{h_m, h_c, h_\alpha\}$ depend on the parameter P. Drop solutions exist for $P^* < P < P_{max}$. At P^*, $h_{max} = h_\alpha$ and the drop structure breaks down in a homoclinic bifurcation.

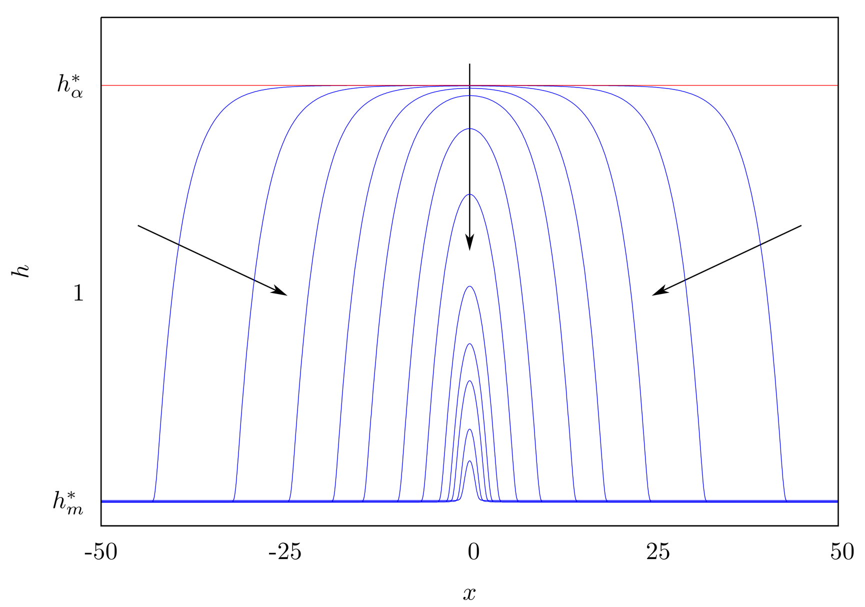


Figure 4: The drop size and shape change as P increases (shown by arrows). Note that the reduced mass m is inversely related to P.

Important observations:

- Drops localized inside $-w < x < w$. Outside of w they decay rapidly to h_m.
- Small drops ($P \gg \sqrt{\alpha}$) look parabolic [Glasner & Witelski 2003].
- Large drops are mesas with $h_{max} < h_\alpha$. "Large" must be defined in terms of both mass and strength of gravity, leading to the mesa parameter

$$\mathbb{M} \equiv \alpha m$$

When $\mathbb{M} \gg 1$, the reduced mass is

$$m(P) = \int_{-\infty}^{\infty} h - h_m \, dx \sim \frac{1}{\sqrt{3}\alpha}\left(\tfrac{1}{2}\ln\alpha - \ln(P - P^*)\right)$$

Multi-drop model

When two or more drops of different pressures P_i exist, a single equilibrium h_m can't be established. There is instead a gradient in the ultra-thin film that causes a flux $\mathcal{J}$ between drops,

$$\mathcal{J}_{R,L} \sim \delta^3 \frac{P_L - P_R}{(X_R - w_R) - (X_L - w_L)}$$

(The full form is easy to find from a quasi-static model of UTF dynamics.)

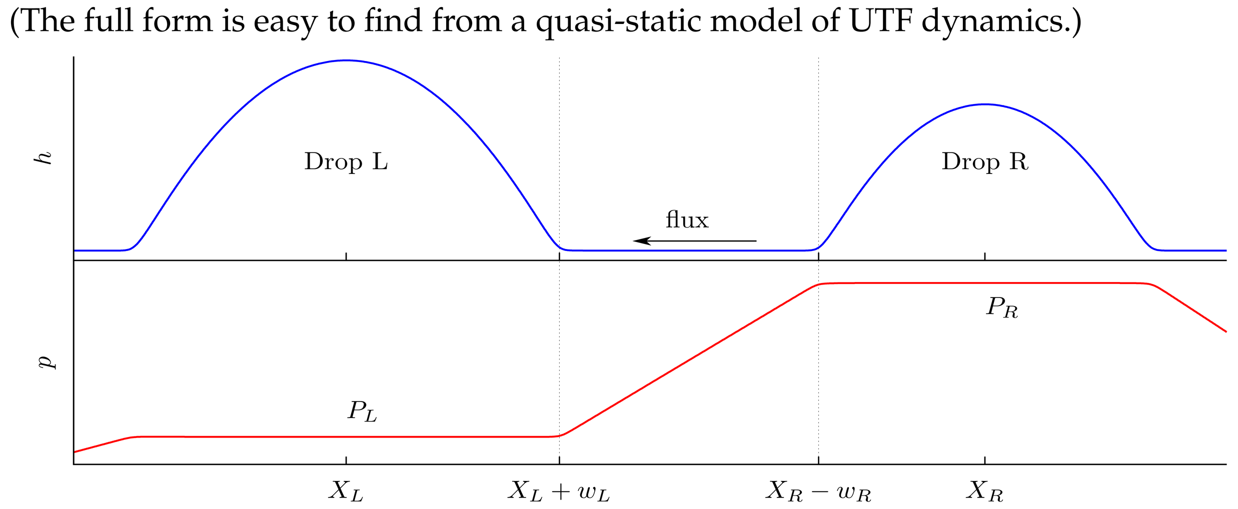


Figure 5: Two drops ("L" and "R") exchange mass through a flux driven by the difference in their pressures.

A model for the evolution of a system of N_0 drops with pressures P_i is

$$\frac{dP_i}{dt} = C_p(P_i)[\mathcal{J}_{i+1,i} - \mathcal{J}_{i,i-1}] \quad \text{where} \quad C_p(P) = \left[\int_{-w}^{w} \frac{\partial h}{\partial P}(x;P)\, dx\right]^{-1}.$$

Derived from:

- Linearizing the lubrication equation about an isolated drop state
- Projecting the result onto the eigenfunctions of the linear operator, but on a finite domain with fluxes $\mathcal{J}$ at the boundaries
- These edge fluxes couple neighboring drop ODEs together
- Assuming widely-spaced drops $\Longrightarrow$ negligible drop motion. Observed for small values of the coarsening parameter

$$\mathbb{K} \equiv \frac{\bar{m}}{\ell\delta} \leq \frac{1}{2}$$

for average reduced drop mass $\bar{m}$ and average drop separation ℓ.

- See [Glasner & Witelski 2003, 2005] for details

In addition to solving P_i equations, we specially deal with vanishing drops. When a drop vanishes, $P_i \to \infty$. To avoid this, we use the rule:

Drop Collapse Rule: If $P_i \geq P_{max}$ at some time, the reduced mass of drop i vanishes and the drop is deleted. Simulation continues with remaining drops.

Self-similar coarsening

We use the model above to simulate drop coarsening. For initial conditions, we choose N_0 initial drops according to

- $X_i = \ell(i-1)$ — Equally spaced,
- $P_i = P(\mathcal{N}(\bar{m}_0, \sigma))$ — Normally distributed in m,

for $i = 1, 2, \ldots, N_0$. This simulates a drop distribution from a dewetting film. The current number of drops $N(t)$ is a good measurement of the progress of coarsening.

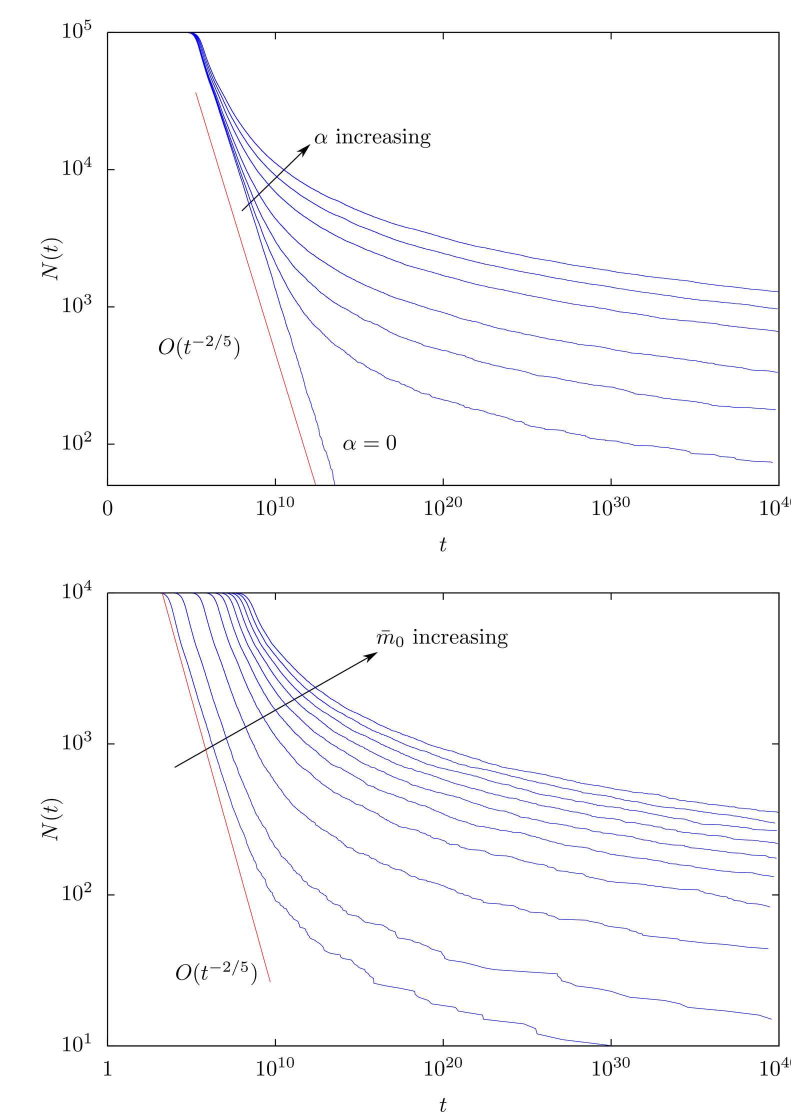


Figure 6: Top: Number of drops $N(t)$, varying α between simulations. Bottom: Number of drops $N(t)$ with fixed $\alpha = 0.1$ and $\mathbb{K} = 0.25$, varying $\bar{m}_0$.

These plots show

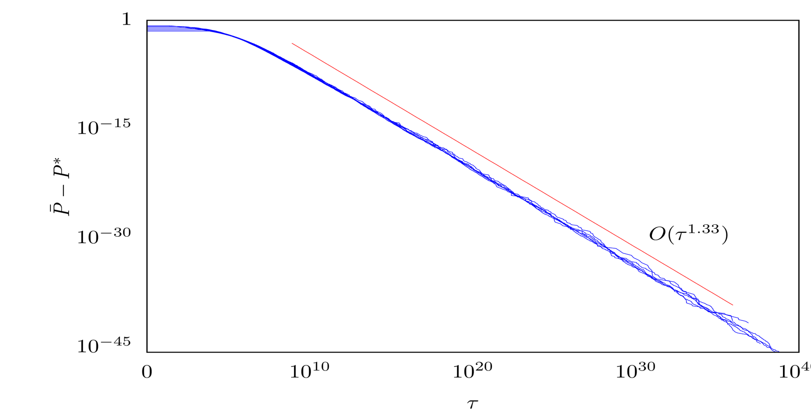
- For $\alpha = 0$ or small $\bar{m}$, $N \propto t^{2/5}$
- When $\bar{\mathbb{M}} = \alpha\bar{m}$ is large, coarsening rate is much, much slower.

Rescale to describe slow coarsening

1. First, adopt convenient timescale motivated by form of dP_i/dt equation,

$$\tau = \frac{t}{T} \quad \text{where} \quad T = \frac{1}{\alpha^2 \mathbb{K}}.$$

2. Next, we observe from simulation that the mean pressure $\bar{P} - P^* \approx \tau^{-1.33}$, see figure below.



3. Combining observation with mass-pressure relation for large drops gives

$$\bar{m}(\tau) \approx \frac{1}{\sqrt{3}\alpha}(1.33\ln\tau + \tfrac{1}{2}\ln\alpha).$$

4. Since mass is conserved, $\bar{m}(\tau)N(\tau) = \bar{m}_0 N_0$, and so for $\tau \to \infty$,

$$N(\tau) \approx \frac{\sqrt{3}\alpha\bar{m}_0 N_0}{1.33\ln\tau + \frac{1}{2}\ln\alpha}, \quad \text{or}$$

$$N \propto \frac{\alpha\bar{m}_0}{\ln\tau} N_0$$

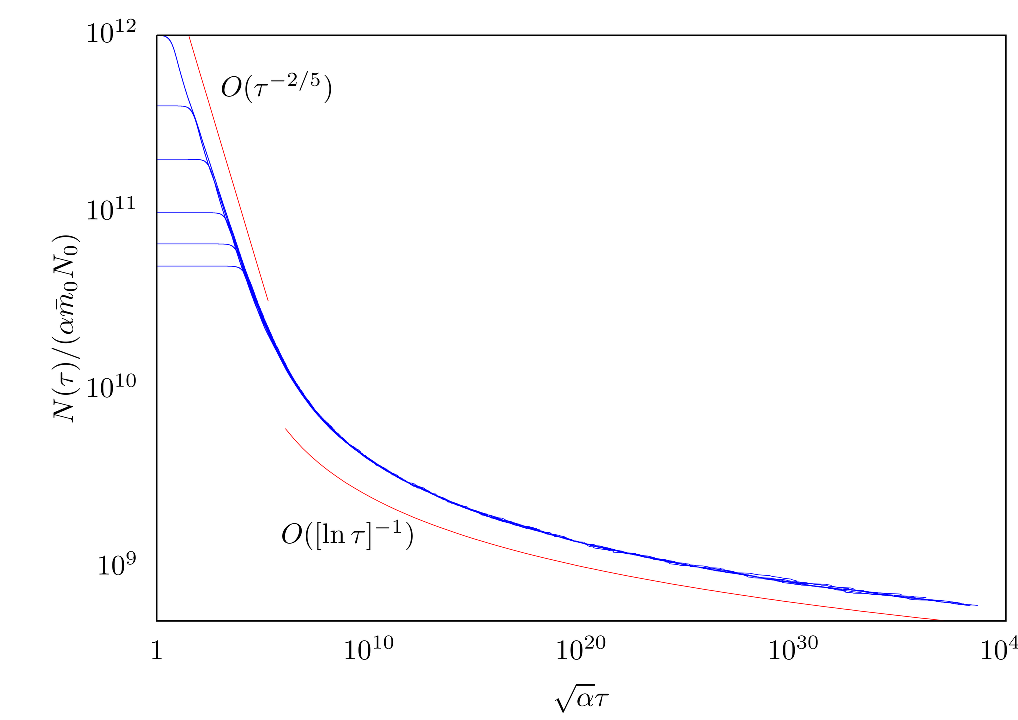


Figure 7: Re-plotting the data from both figures above using the timescale T and scaling the number of drops appropriately shows all curves collapsing onto one trend.

Notice:

- For early times, the behavior follows the $\tau^{-2/5}$ power-law.
- For later times, the $1/\ln\tau$ log-law behavior dominates.
- This coarsening corresponds to $\bar{\mathbb{M}} = \alpha\bar{m}(t)$ of the mean drop increasing as $\bar{m}(t)$ increases.
- Vertical scale is adjusted by the mesa parameter calculated using the total active system mass $\bar{m}_0 N_0$.

Discussion

This work describes collapse-dominated coarsening with the effects of gravity included. As coarsening progresses:

- The number of drops decreases while the total mass is conserved
- The size of the mean drop grows
- $\bar{\mathbb{M}}$ grows
- The average drop becomes more mesa-like in shape
- Coarsening slows down from $\mathcal{O}(t^{-2/5})$ to $\mathcal{O}(\frac{1}{\ln t})$.

Collision-dominated coarsening, $\mathbb{K} \gtrsim 1$, may behave differently with new types of collisions possible for $\alpha > 0$.

Additional information and acknowledgments:

M.B. Gratton and T.P. Witelski, Coarsening of unstable thin films subject to gravity. *Phys. Rev. E*, 77:016301, 2008.

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