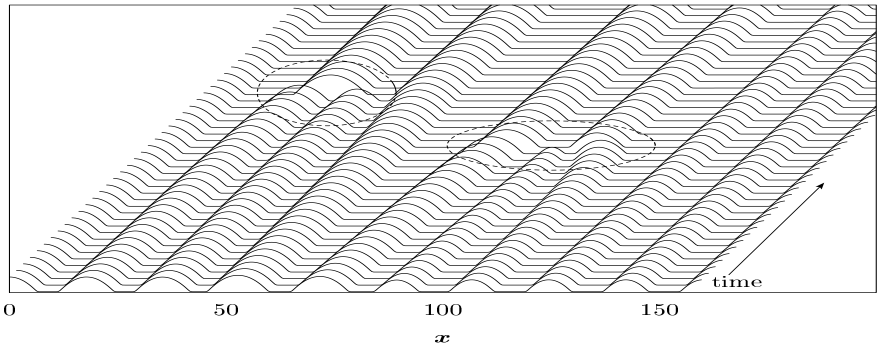
Coarsening Dynamics of Dewetting Fluid Films



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Work with Karl Glasner (U-Arizona) and Michael Gratton (Duke⟶Northwestern)

- Lubrication models of viscous fluid films coating solids
- Multi-scale dynamics controlled by *materials properties* and *surface chemistry*
- **Dewetting**: pattern forming instabilities

  Break-up of fluid layers into arrays of localized droplets
- Long-time asymptotic behavior: **Coarsening**

  Re-grouping of small droplets into larger masses
- Deriving reduced models: lower-dimensional dynamical systems

  Coupled ODEs for arrays of interacting droplets
- Modes of coarsening: collapse and collision events **[micro]**
- A statistical scaling law for large arrays **[meso]**
- Influences at the macro-scale – a scaling transition **[macro]**

Dewetting:

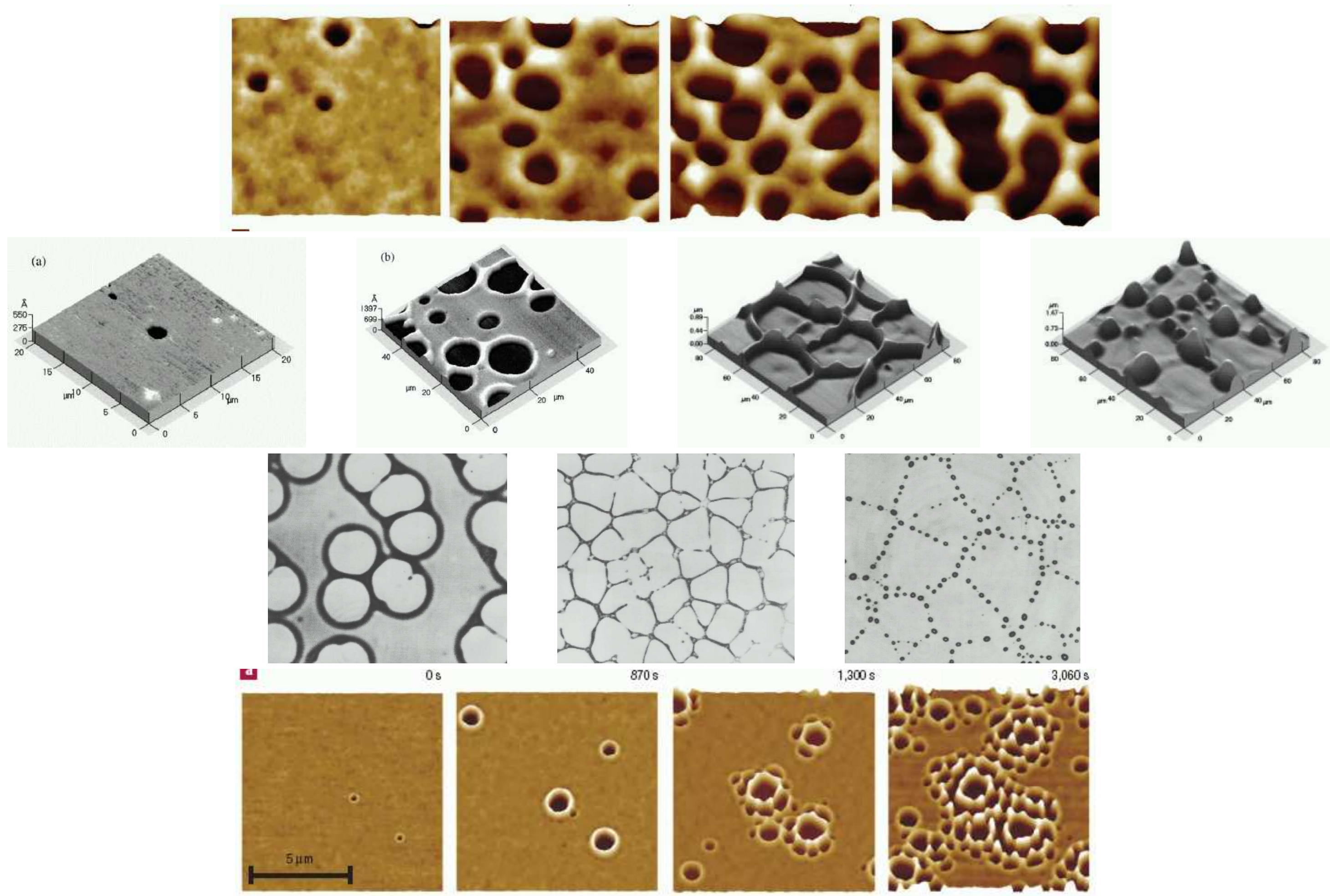
The instability of uniform coatings of viscous fluids on solid surfaces.

Very undesirable for most applications **(painting, printing, microfluidic devices)**.

Observed non-uniformities in experiments for polymer films on SiO

Holes ⟶ complex patterns **(fractals?)** ⟶ polygonal ridges ⟶ droplets

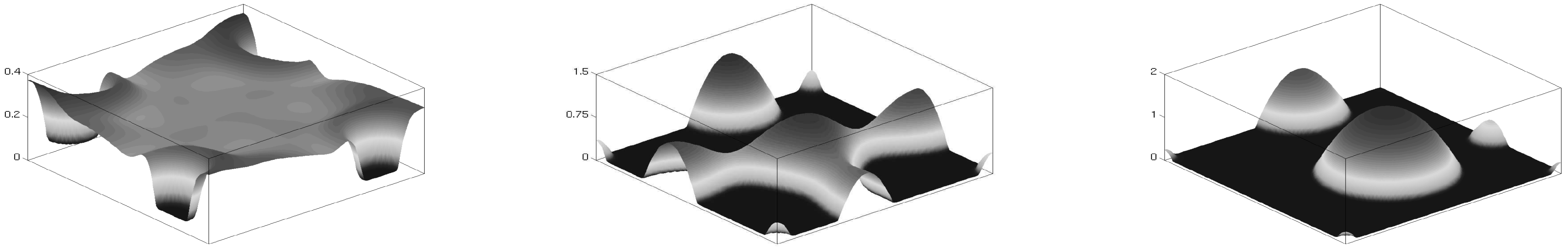
Increasing time ⟶



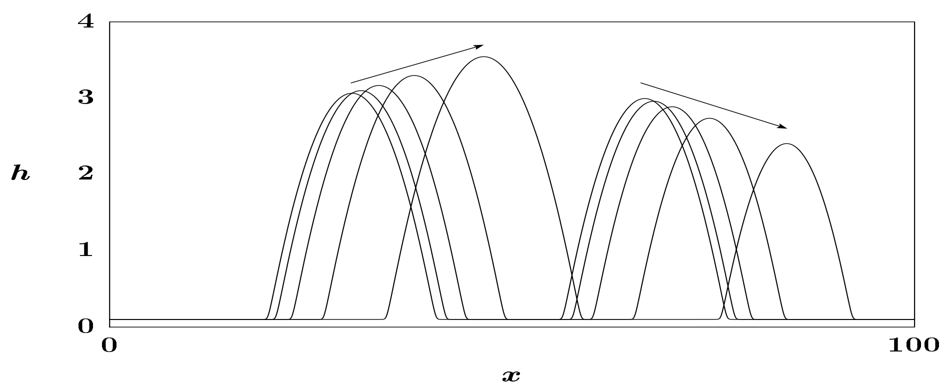
[J. Becker et al, 2002] [P. F. Green et al, 2001] [A. Sharma & G. Reiter, 1996]

Dewetting

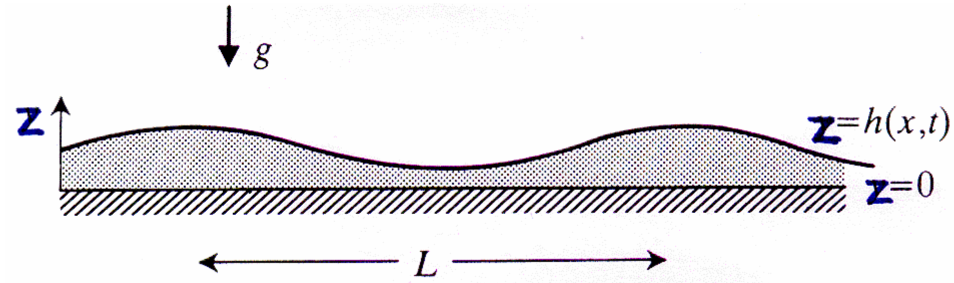
- Early stages: linear instability, rupture, and drop formation. Phase separation of droplets and ultra-thin films, called *spinodal dewetting*.



- Later stages: each drop is locally near equilibrium, but the collection is globally far-from-equilibrium.
  Produces slow, quasi-steady evolution: **coarsening dynamics**.
  Energetically driven successive rearrangements: evolution of drop positions and masses.



Classical lubrication models for fluid dynamics of thin films



Fluid volume: $\quad 0 \le x, y \le L \qquad 0 \le z \le H(x,y,t)$

- Navier-Stokes eqns: velocity field $\vec{\mathbf{u}}$ for viscous incompressible flow

$$\mathrm{Re}\frac{D\vec{\mathbf{u}}}{Dt} = -\nabla p + \nabla^2 \vec{\mathbf{u}} \qquad \nabla \cdot \vec{\mathbf{u}} = 0$$

- Low Reynolds number creeping flow limit (Stokes flow)

$$\vec{0} = -\nabla p + \nabla^2 \vec{\mathbf{u}} \qquad \nabla \cdot \vec{\mathbf{u}} = 0$$

- Asymptotics in the aspect ratio, $\delta = H/L \to 0$
- Boundary conditions at $z = 0$ and $z = h(x,y,t)$

The Reynolds lubrication equation in 1-D

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

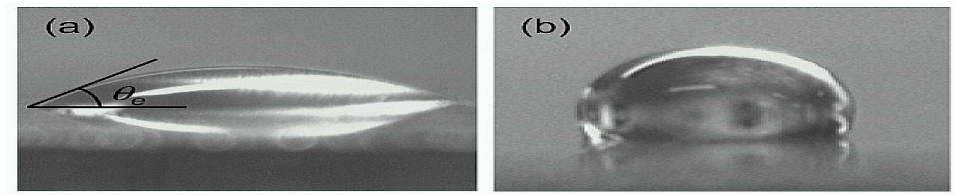
$h = h(x,t)$: film thickness

$J = -h^3 \partial_x p$: mass flux

$p = p[h]$: dynamic pressure

Dominant physics for thin viscous coatings:

- Neglect gravity for very thin films*
- Strong surface tension
- Physio-chemical fluid-solid intermolecular interactions (Van der Waals, ...) determining wettability and contact angles



wetting **non- or partially wetting**

The pressure model

Disjoining pressure $\Pi(h)$, Linearised surface tension $\rightarrow$ $p = \Pi(h) - \frac{\partial^2 h}{\partial x^2}$

The dewetting model

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(h^3 \frac{\partial}{\partial x}\left[\Pi(h) - \frac{\partial^2 h}{\partial x^2}\right]\right)$$

"Balanced" Van der Waals forces [L. W. Schwartz et al, others]

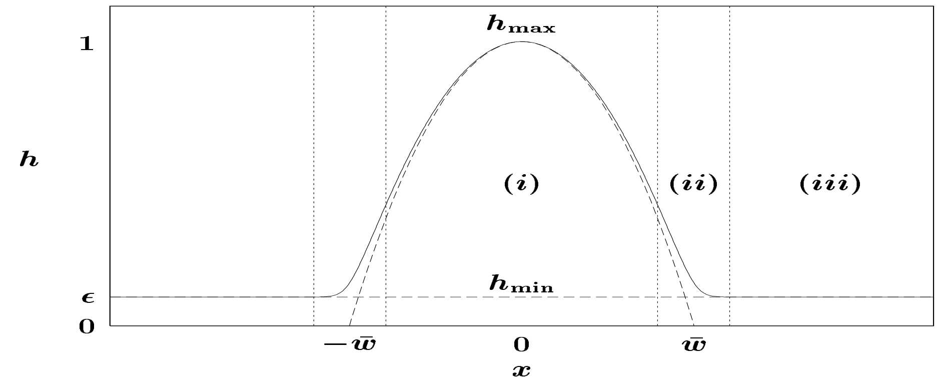
$$\Pi(h) = \frac{1}{\epsilon}\left(\frac{\epsilon}{h}\right)^3\left[1 - \left(\frac{\epsilon}{h}\right)^m\right] \qquad m \geq 1$$

$h = \epsilon > 0$: sets scale for equilibrium ultra-thin film (UTF)

Localized steady state solutions: 1-D droplets, constant $p \equiv P$

$$h = H(x;P)$$

$$\boxed{\frac{d^2H}{dx^2} = \Pi(H) - P}$$



Properties and asymptotic structure for $\epsilon \to 0$

(i) Droplet core: parabolic profile for $|x| \ll \bar{w}$

$$\boxed{H(x) \sim \tfrac{1}{2}P(\bar{w}^2 - x^2)}$$

(ii) Contact line: matching determines width and contact angle

$$\left.\frac{dH}{dx}\right|_{x\to-\bar{w}} \equiv A = \sqrt{2|U(\epsilon)|} \quad\Longrightarrow\quad \bar{w}(P) = \frac{A}{P}$$

Droplet mass $\sim$ mass of core region: $$\bar{m}(P) = \int_{-\bar{w}}^{\bar{w}} H(x)\,dx \sim \frac{2A^3}{3P^2}$$

(iii) Ultra-thin film: in outer region $|x| \gg \bar{w}$: $$H \sim h_{\min}(P) \sim \epsilon + \epsilon^2 BP$$

Dynamics of a single droplet: Model IBVP problem

$$\frac{\partial h}{\partial t} = \partial_x (h^3 \partial_x [\Pi(h) - \partial_{xx} h]) \qquad -L \le x \le L$$

Droplet IC: $h(x, 0) = H(x; P_0)$

Imposed flux BCs: $J \equiv -h^3 \partial_x p \qquad J(-L) = \sigma \tilde{J}_- \qquad J(L) = \sigma \tilde{J}_+$

- Small fluxes set a slow timescale, $\sigma \ll 1$: $\boxed{\tau = \sigma t}$
- Fluxes drive slow evolution

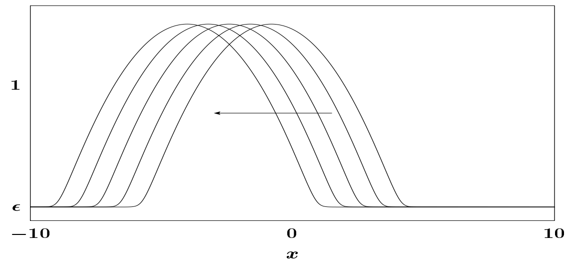
$$h(x, t) = \boxed{H(x - X(\tau); P(\tau))} + \sigma h_1(x, \tau) + O(\sigma^2)$$

$X(\tau)$: position, $X(0) = 0 \qquad P(\tau)$: pressure, $P(0) = P_0$

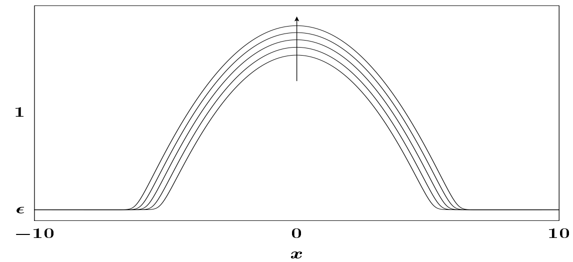
- Two evolution eqns per drop derived from the solvability conditions for h_1

$$\boxed{\frac{dX}{dt} = -C_X(P)(J_+ + J_-) \qquad \frac{dP}{dt} = C_P(P)(J_+ - J_-)}$$

Drift mode : $J_+ = J_-$

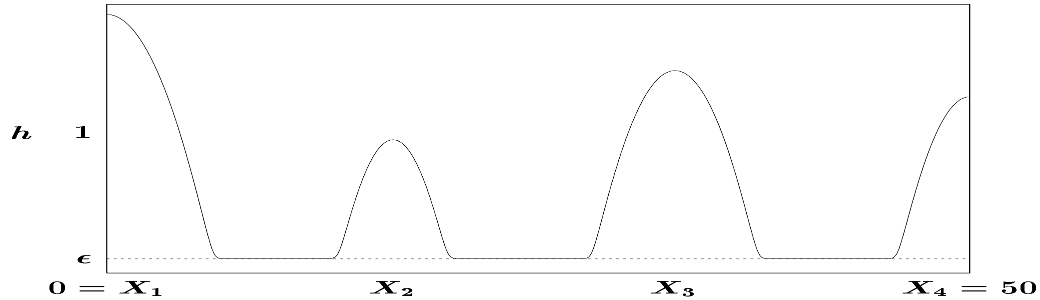


Growth mode : $J_+ = -J_-$

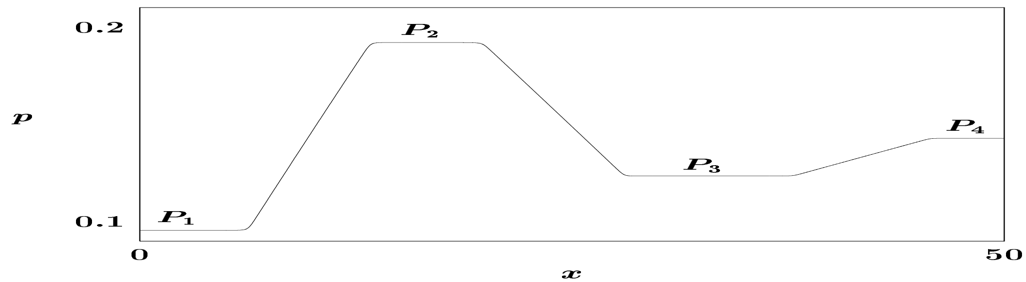


Dynamics of arrays of droplets

- A set of drops at positions X_k for $k = 1, 2, \cdots, N$



- Each isolated droplet has a locally uniform pressure P_k



- Differences in the pressures will generate fluxes in the UTF
- UTF layer between drops: almost flat, quasi-static.

  The flux is the gradient of a potential function

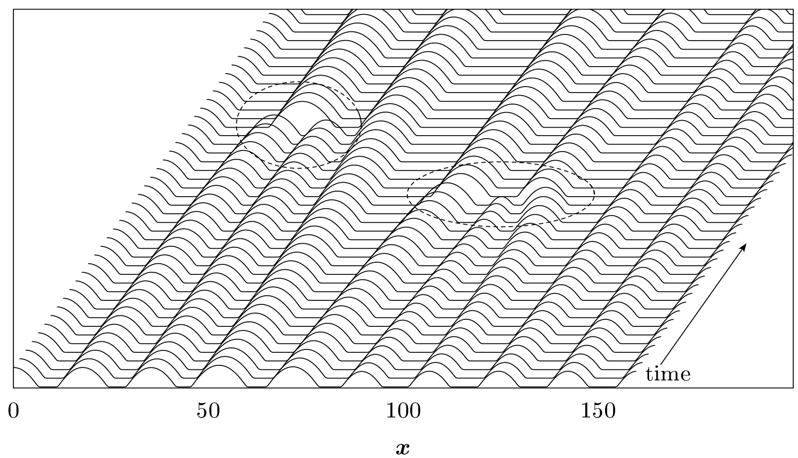
$$J = -h^3 \Pi'(h) h_x \equiv -\partial_x V(h).$$

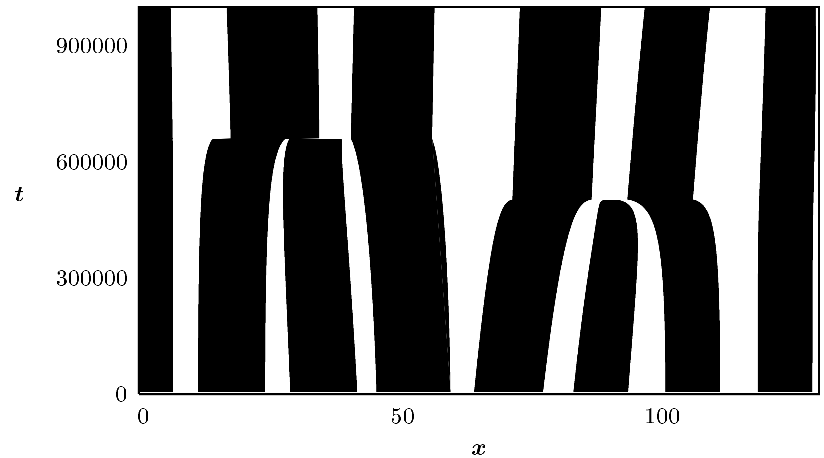
- Flux between neighbors: $$J_{k,k+1} = -\frac{V(h_{\min}(P_{k+1})) - V(h_{\min}(P_k))}{[X_{k+1} - \bar{w}(P_{k+1})] - [X_k + \bar{w}(P_k)]}$$
- Array evolution equations:

$$\frac{dP_k}{dt} = C_P(P_k)(J_{k,k+1} - J_{k-1,k}) \qquad \frac{dX_k}{dt} = -C_X(P_k)(J_{k,k+1} + J_{k-1,k})$$

Dynamics of arrays of droplets (II)

PDE simulations: droplet movement "world-lines"





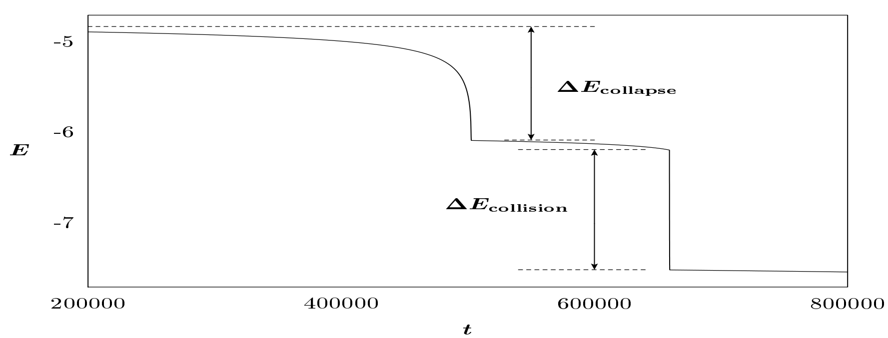
Observe two classes of *coarsening* events:

- **Collapse**: 1 drop → 0 drops
- **Collision**: 2 drops → 1 drop

Dissipation of energy

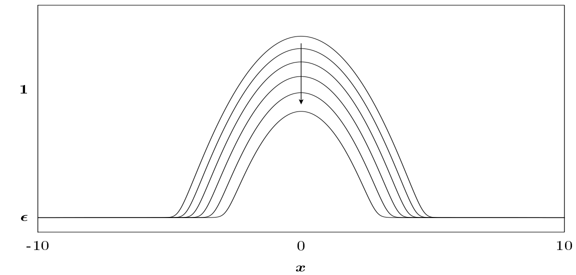
$$E(h) = \int U(h) + \tfrac{1}{2}h_x^2\,dx \quad \longrightarrow \quad \frac{dE}{dt} = -\int h^3 p_x^2\,dx \le 0$$

Favors fewer larger drops over many smaller ones → coarsening



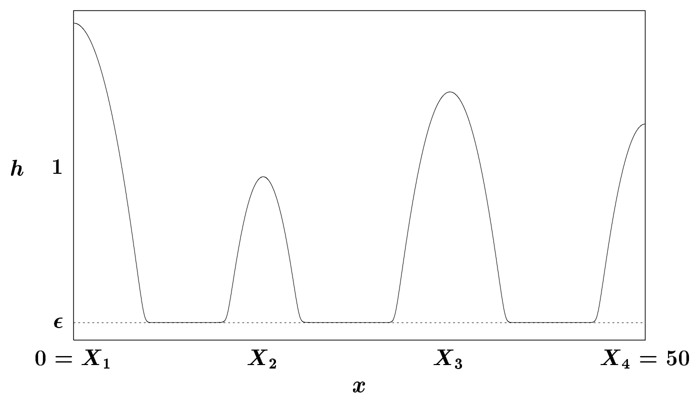
Collapse: small drops "melt" into the surrounding film as $\text{Mass}_k \to 0$

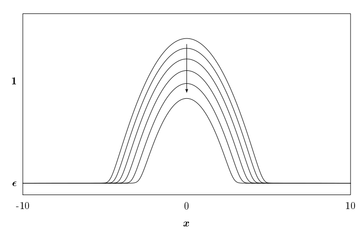
$\Longrightarrow$ $P_k \nearrow p_{\max}$ for at finite time $t \to t_c$:



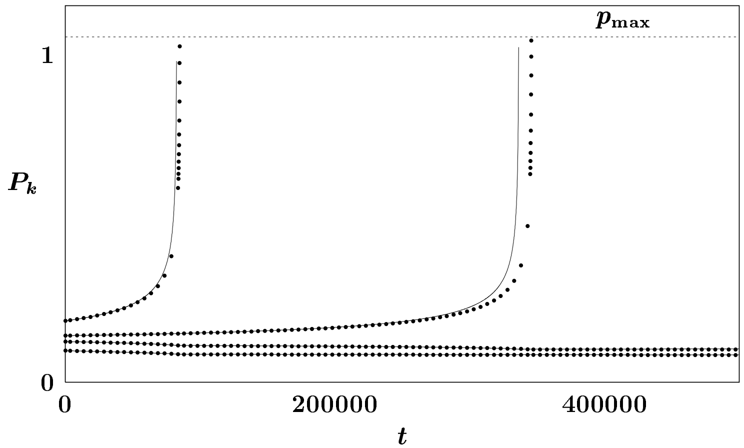
$$\frac{dP_k}{dt} \propto P_k^3 \quad \to \quad P_k(t) = O([t_c - t]^{-1/3})$$

Initial Conditions





Evolution of Pressures



[PDE results (dots), ODE model (curves)]

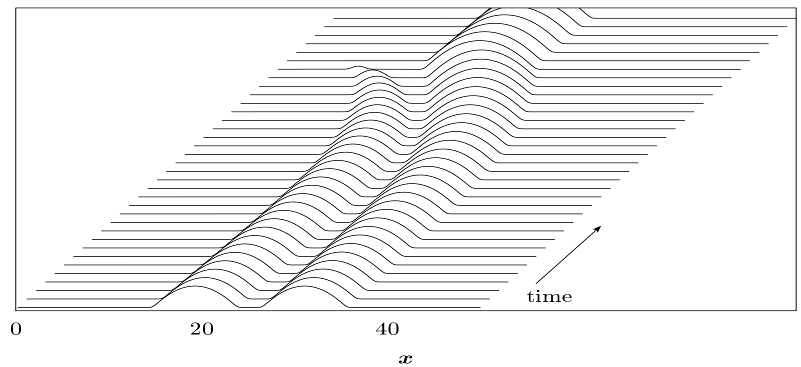
- Smaller drops tend to collapse first
- Larger drops tend to grow a little and become more stable

a la *"Survival of the Fattest"* in other coarsening [Rubinstein & Sternberg, 1992]

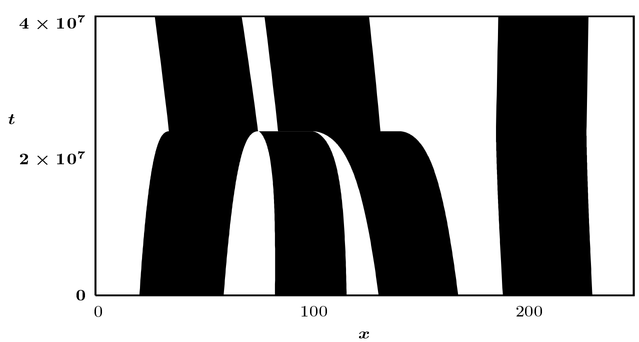
Collision: Merging of drops as separation distance vanishes,

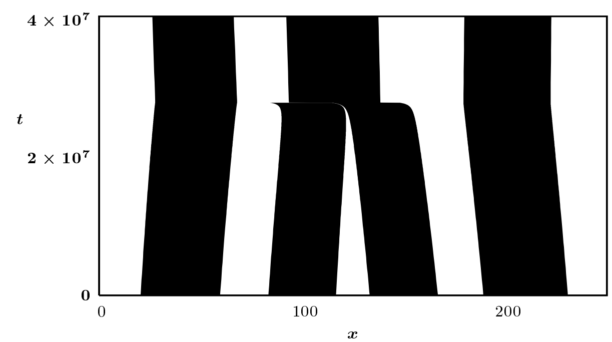
$$D_{k,k+1} \equiv [X_{k+1} - \bar{w}(P_{k+1})] - [X_k - \bar{w}(P_k)] \to 0$$

- Collision requires the interactions of 3 or more drops, 2 drops alone will NOT collide

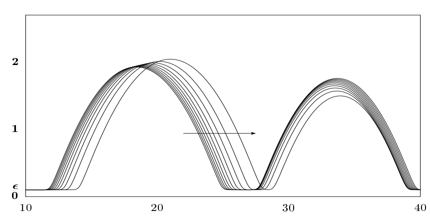


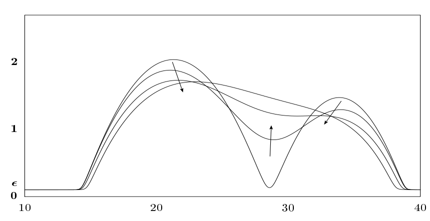
- But, generically only 2 drops can merge at a time **[Analysis of 4-drop ODE model]**

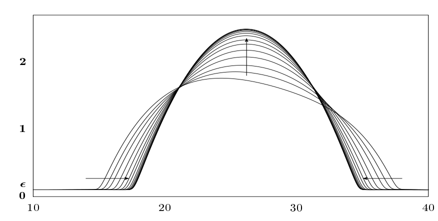




- Very brief far-from-equilibrium dynamics of merging: $\mathbf{2 \to 1}$ drops







t^-_{collide} t^+_{collide}

Coarsening dynamical system =

Near-equilibrium ODE system + Coarsening rules

[Krüg et al (2002), Watson et al (2003), others]

- For $O(1) \ll t < t_1$

$$\left\{ \frac{dX_k}{dt} = \cdots \qquad \frac{dP_k}{dt} = \cdots \right\} \qquad k = 1, 2, \cdots, N$$

- At $t = t_1^-$, the soln of ODEs satisfies a *detection condition*. Stop the ODEs. Enforce collision or collapse. Create new IC's at $t = t_1^+$ for remaining $(N-1)$ drops via *coarsening rules* for collision or collapse:

$$\left\{ X_k(t_1^+) = \cdots \quad P_k(t_1^+) = \cdots \right\} \quad k = 1, 2, \cdots, N-1$$

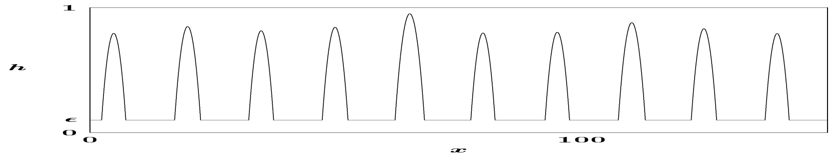
- For $t_1^+ \le t < t_2$

$$\left\{ \frac{dX_k}{dt} = \cdots \qquad \frac{dP_k}{dt} = \cdots \right\} \qquad k = 1, 2, \cdots, N-1$$

- At $t = t_2^-$ another coarsening event detected...
  and repeat, $N \to (N-1) \to (N-2) \to \cdots$

Coarsening in large arrays

Consider a problem with a large number of drops, $N \gg 1$



How does $N(t)$ evolve? Should we expect mostly collision or collapse events?

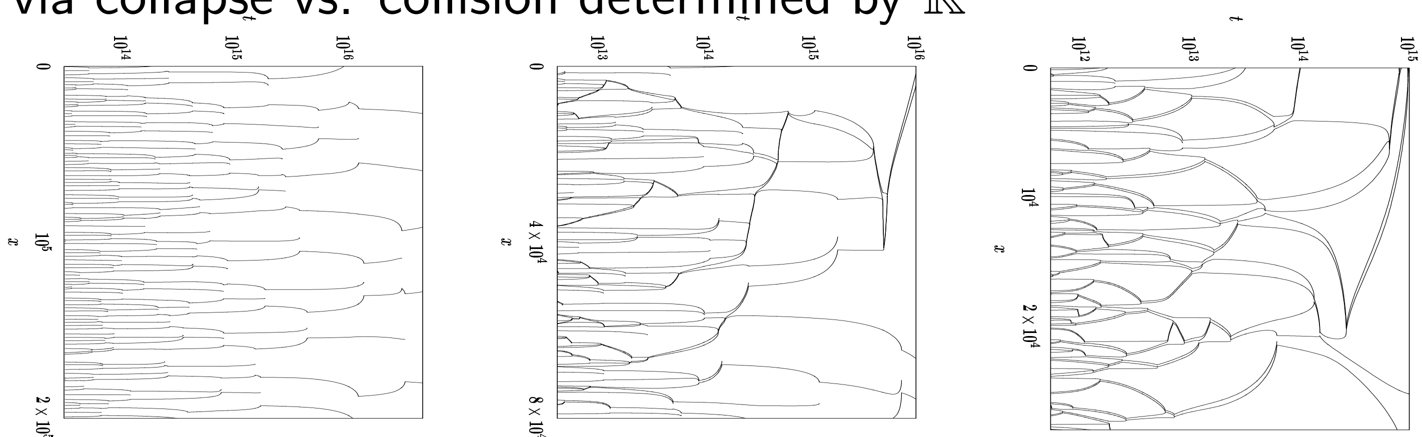
Define characteristic film thickness

$$H_c \equiv M/L = \text{avg height (film mass per unit length)}$$

Scaling analysis of ODEs in *dilute limit* yields control parameter

$$\mathbb{K} \equiv H_c/\epsilon = \text{“}\underline{\text{Coarsening ratio}}\text{”} \approx C_X/C_P \sim \frac{\textbf{Collide}}{\textbf{Collapse}}$$

Coarsening via collapse vs. collision determined by $\mathbb{K}$

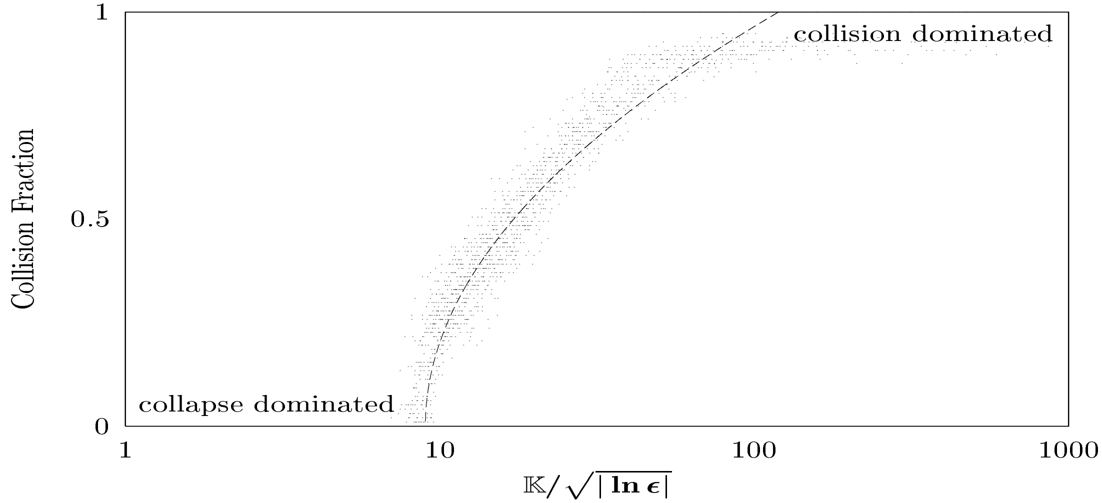


$\mathbb{K}_1 < \mathbb{K}_2 < \mathbb{K}_3$

All collapses ... All collisions

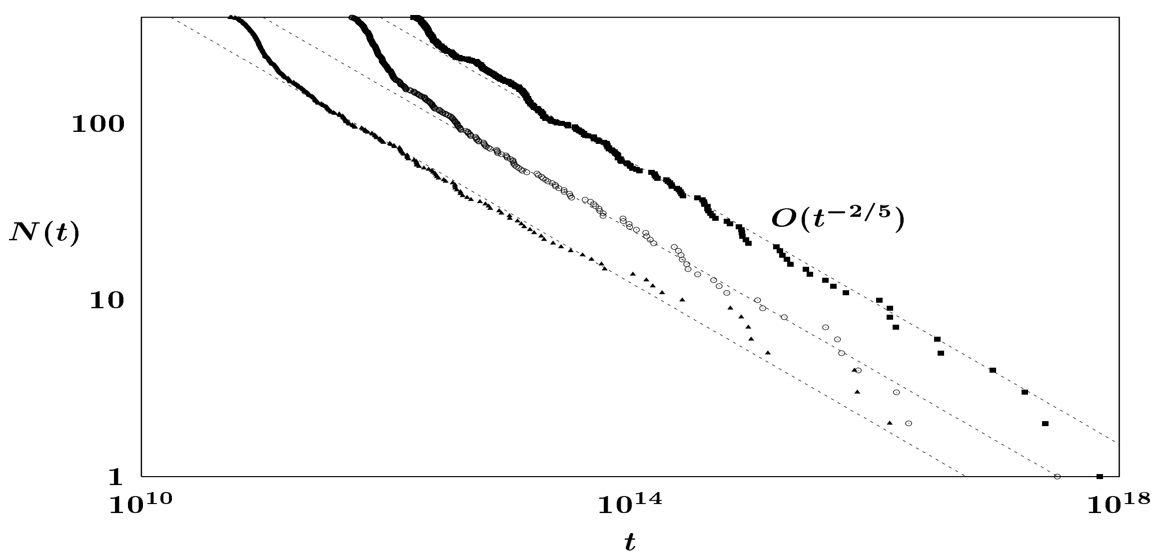
Coarsening in large arrays

Collision fraction: fraction of events that are collisions



Independent of $\mathbb{K}$, coarsening rate via assumptions of local, independent events:

$$\boxed{N(t) \sim O(t^{-2/5})} \qquad t \to \infty$$



Coarsening in macroscopically large arrays

Imagine starting with

- $N_0 = 10^{100}$ tiny parabolic drops (gravity is negligible)
- Wait for a looooooong time, coarsening eventually leads to:

The final state is a *single drop*:

- It containing the entire mass of the system
- For large N_0, it would be implausibly big and tall
- Tall $\implies$ violates "gravity negligible" assumption
- Include a gravity term:

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(h^3 \frac{\partial}{\partial x}\left[\Pi(h) - \frac{\partial^2 h}{\partial x^2} + \alpha h\right]\right) \qquad \alpha = \frac{\text{Gravity}}{\text{VdW}}$$

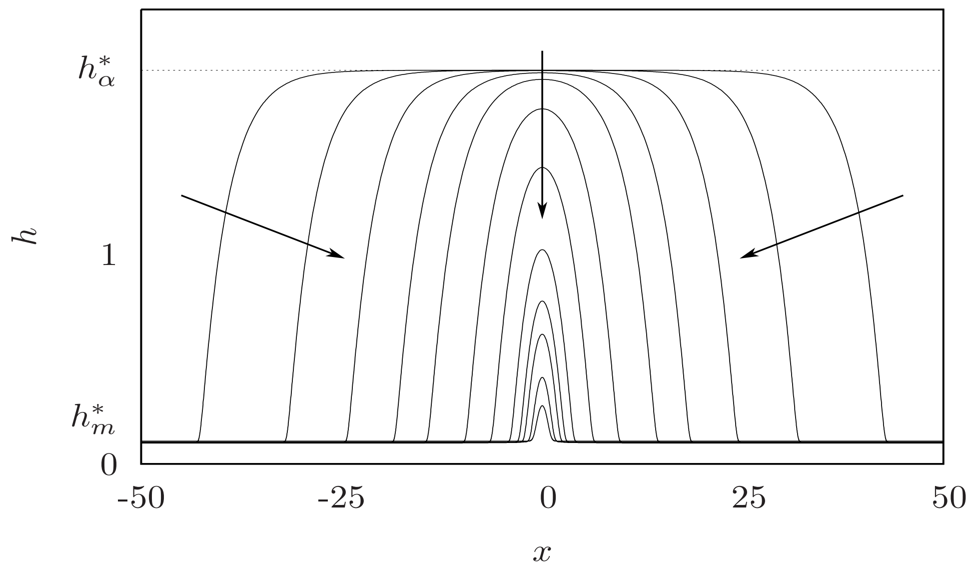
$\alpha \approx 10^{-9} - 10^{-7}$

$\alpha h = O(1)$ when h becomes large...

Coarsening with gravity (I)

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

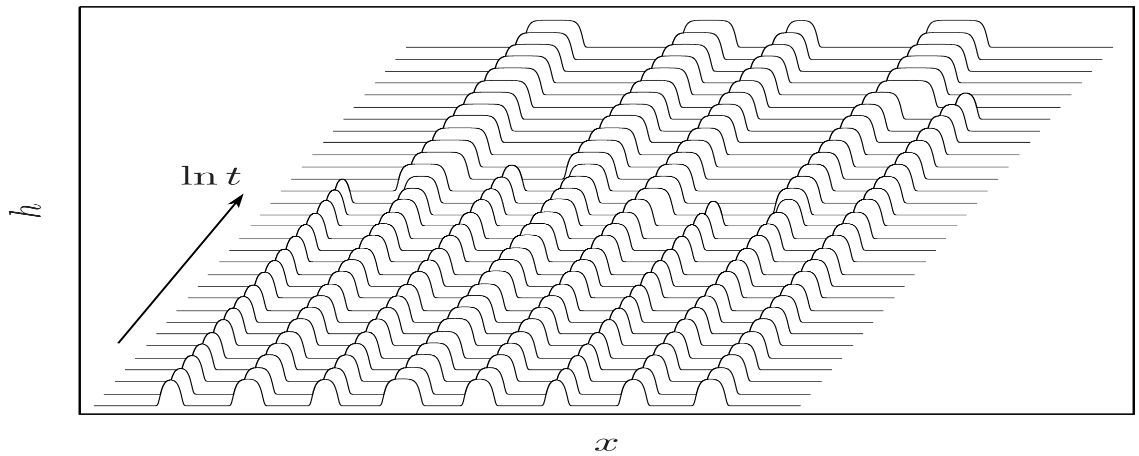
- Family of droplet solutions has two limiting forms
- For small mass ($m \to 0$) drops are small and still take parabolic form
- For large mass ($m \to \infty$) gravity sets a maximum height, h_α.
  Height saturates, drops become wide "*pancakes*", "*puddles*" or "*mesas*"



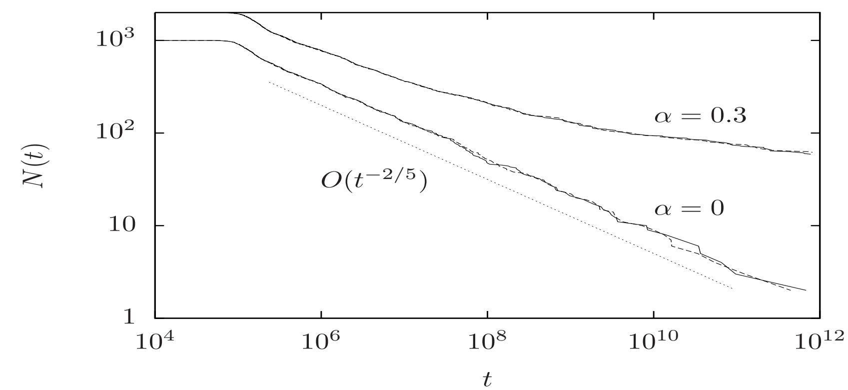
- Define a "Mesa parameter": $M = m\alpha$

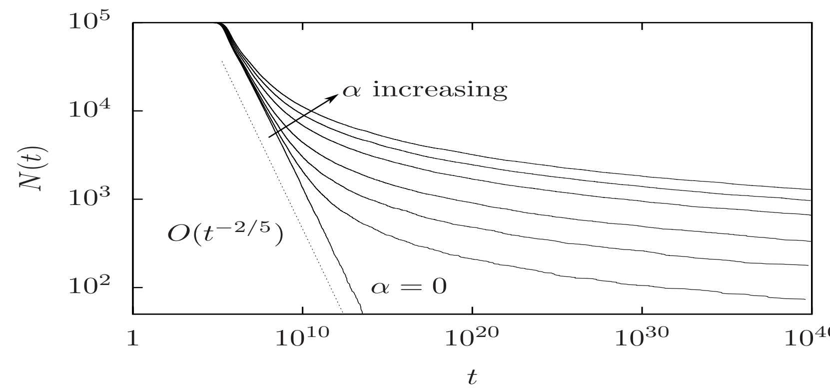
$M \ll 1:$ parabolic drop $\qquad$ $M \gg 1:$ mesa drop

Coarsening with gravity (II)

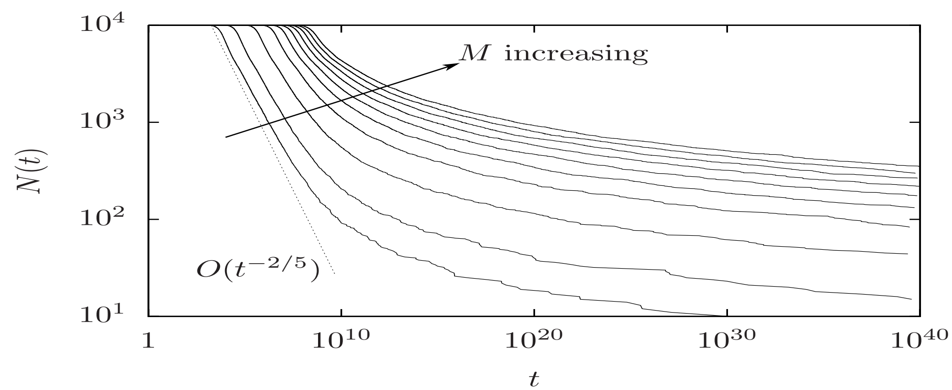


- Increasing gravity (α) slows the rate of coarsening

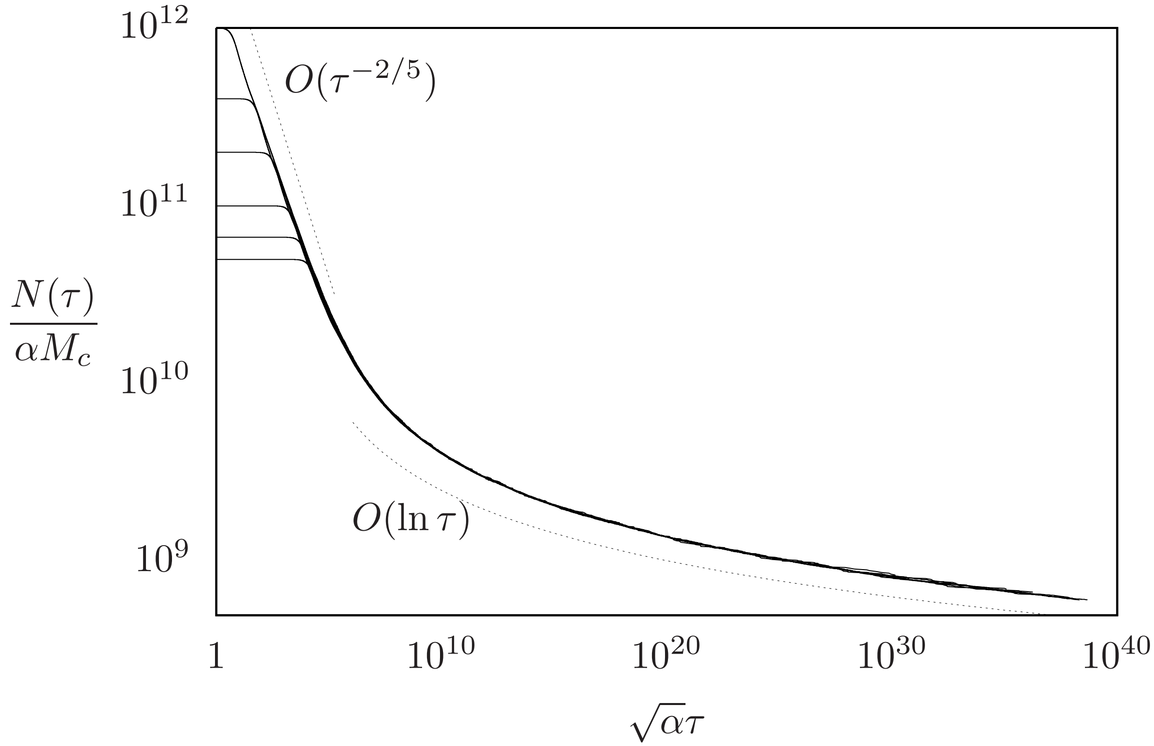




- Similarly, by increasing initial drop size, with α fixed



Coarsening with gravity (III) With appropriate rescaling, can collapse all to:



A transition to a slower gravity-dominated coarsening law:

$$N(t) \approx O(t^{-2/5}) \qquad \longrightarrow \qquad N(t) \approx O(1/\ln t)$$

Further studies

- New work on the rigorous estimates for an upper bound on the coarsening rate by Otto, Rump & Slepčev as a gradient flow in the Wasserstein metric (optimal transport theory)
- Further work
  - Rigorous bounds on short-time nonlinear instabilities (with H.-J. Hwang (2005))
  - Influence of evaporation or condensation (breaking of conservation of mass)
  - Influence of convective driving forces (symmetry breaking via gravity or thermal forcing)
  - Influence of thermal effects (stochastic forcing) (a la Stone et al (2005), Grün et al (2005))
  - Influence of slip conditions (with Münch & Wagner (2005))
  - Further study of intermediate-time behavior connecting rupture to hole-growth regimes and extensions to 2-D
  - Further studies of coarsening in unstable discrete dynamical systems to model granular materials and image processing