Spreading and bi-stability of droplets driven by thermocapillary and centrifugal forces

Joshua Bostwick
North Carolina State University

Workshop on Surfactant Driven Thin Film Flows
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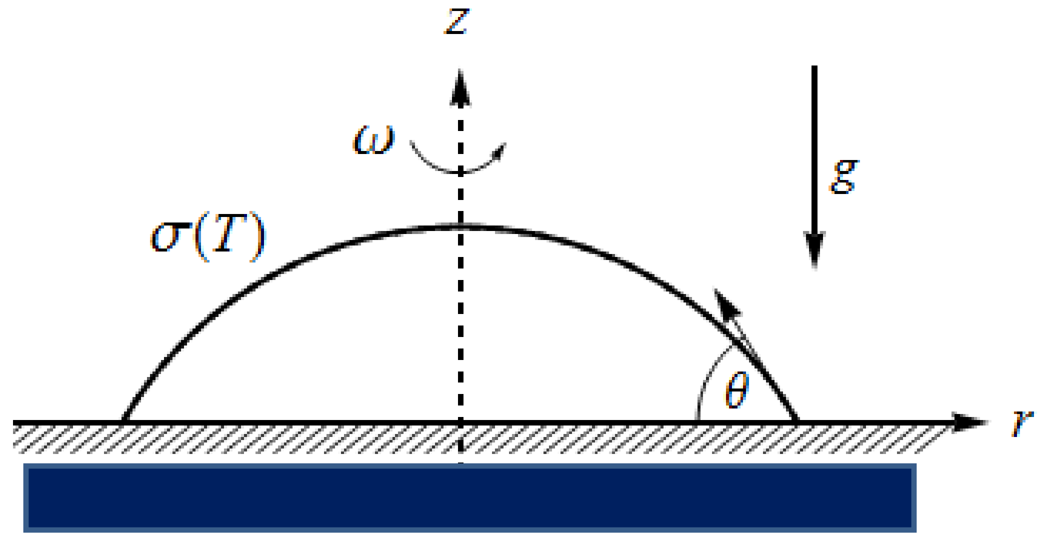
Outline

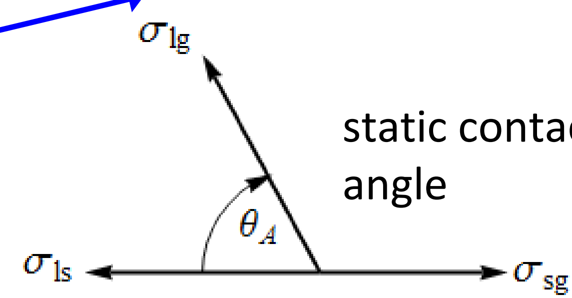
- Definition sketch
  - Spreading mechanisms
    - thermocapillarity
    - wetting vs. spreading
- Quasi-static spreading
  - axial vs. radial thermal gradients
    - flows, interface shapes and spreading rates
  - bi-stability
    - competition
  - effect of applied temperature profile
    - linear vs. logarithmic heating

Why do fluids spread?



- Spreading forces
  - Body
    - gravity, centrifugal
  - Surface
    - thermocapillarity
  - Contact
    - wetting

<u>Young-Dupre’</u>

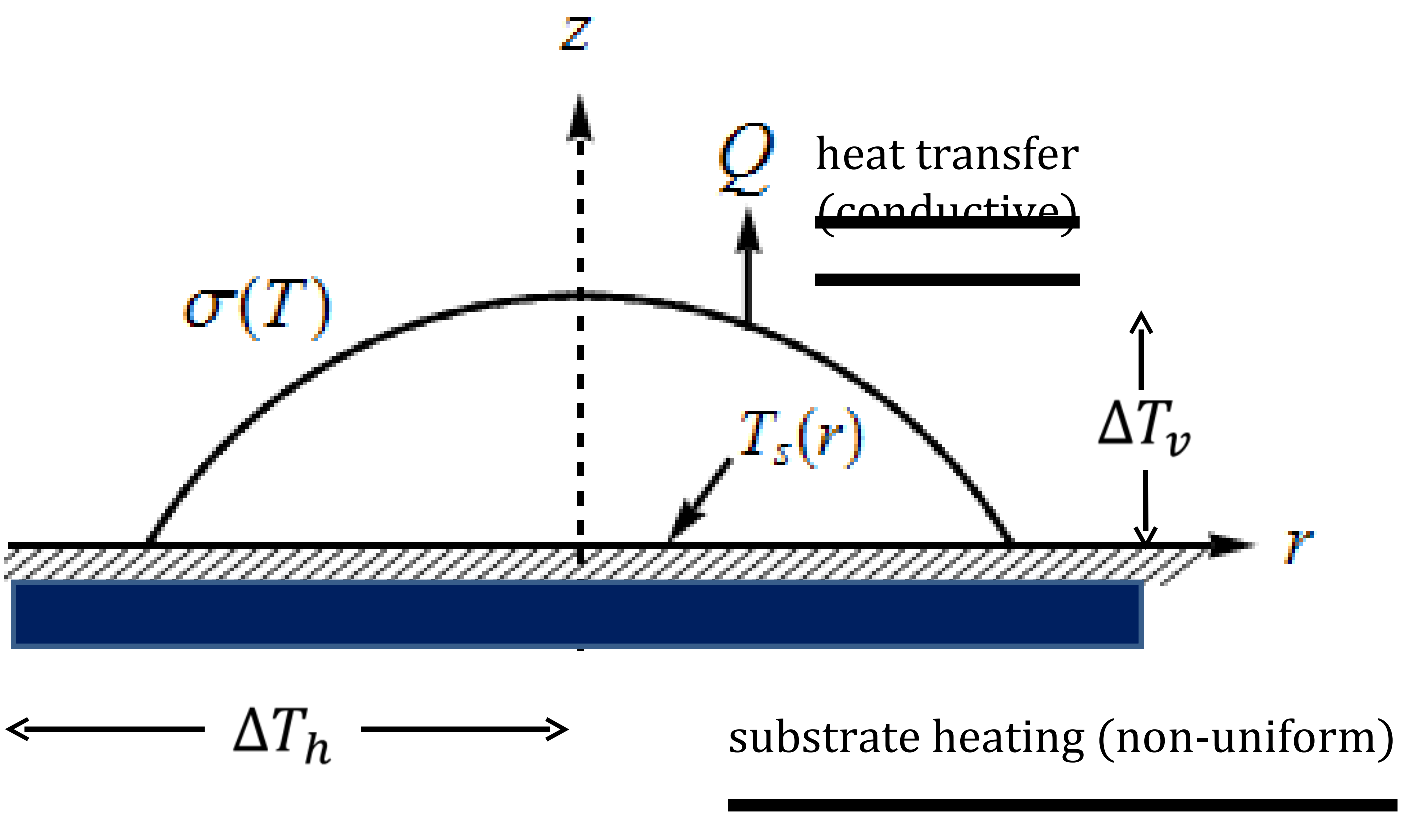


static contact-angle

- Competition can lead to instabilities!

Heating conditions

motivated by experiments in Behringer group (Duke University)



NOTE: 2 temperature scales $\Delta T_h + \Delta T_v$

Thermocapillary forces

surface tension equation of state

$$\sigma = \sigma_0 - \gamma\,(T - T_0)$$

Marangoni stress (shear)

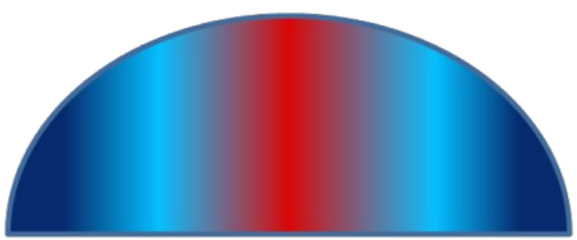
$$\tau \propto \nabla T$$

substrate heating (non-uniform)

$$T_s(r) \longrightarrow \nabla T \sim \frac{\Delta T_h}{\Delta r}$$

heat transfer (conductive)

$$Q \propto \Delta T_v \longrightarrow \nabla T \sim \frac{\Delta T_v}{\Delta z}$$



<u>radial gradient</u> $(\hat{N})$

<u>axial gradient</u> $(\hat{M})$

wetting vs. spreading

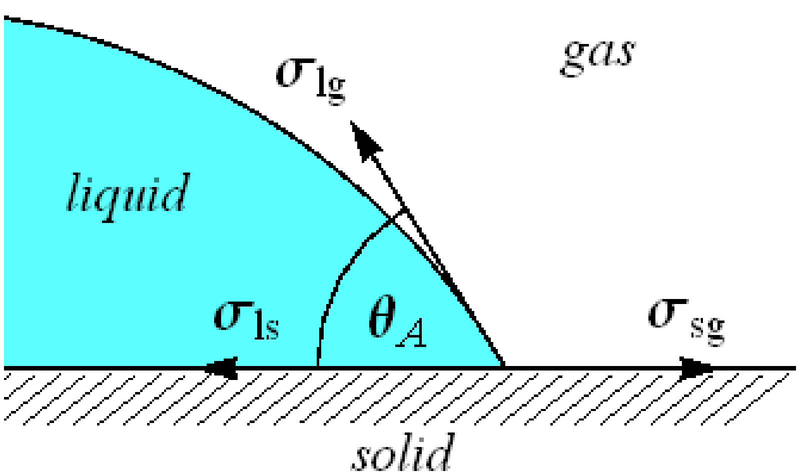
modeling microscopic effects using macroscopic quantities

wetting

Young-Dupre equation

force balance (statics)

$$\sigma_{sg} - \sigma_{ls} \equiv \sigma_{lg} \cos\theta_A$$



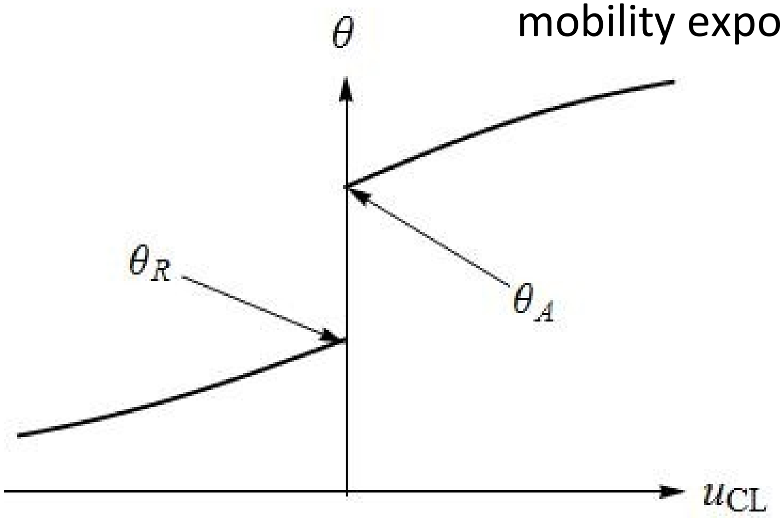
spreading

dynamic contact-line law

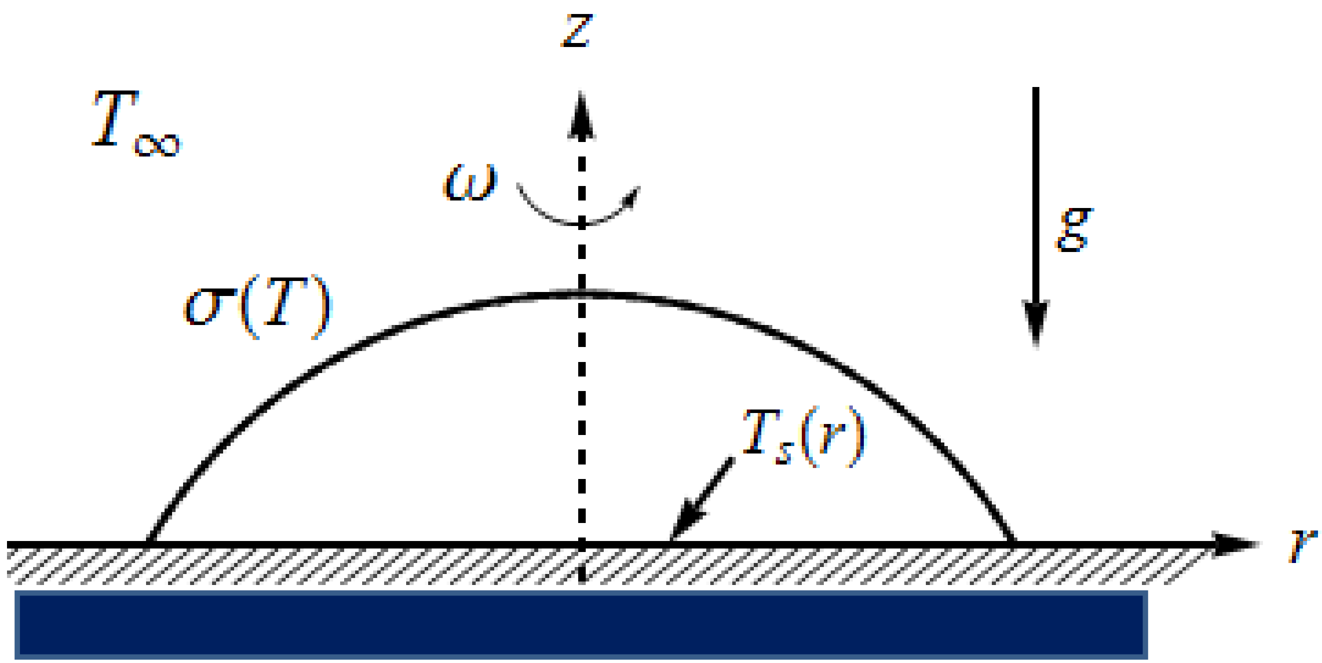
force imbalance (dynamics): $F \sim (\theta - \theta_A)$

$$u_{CL} = (\theta - \theta_A)^m$$

mobility exponent



Definition sketch



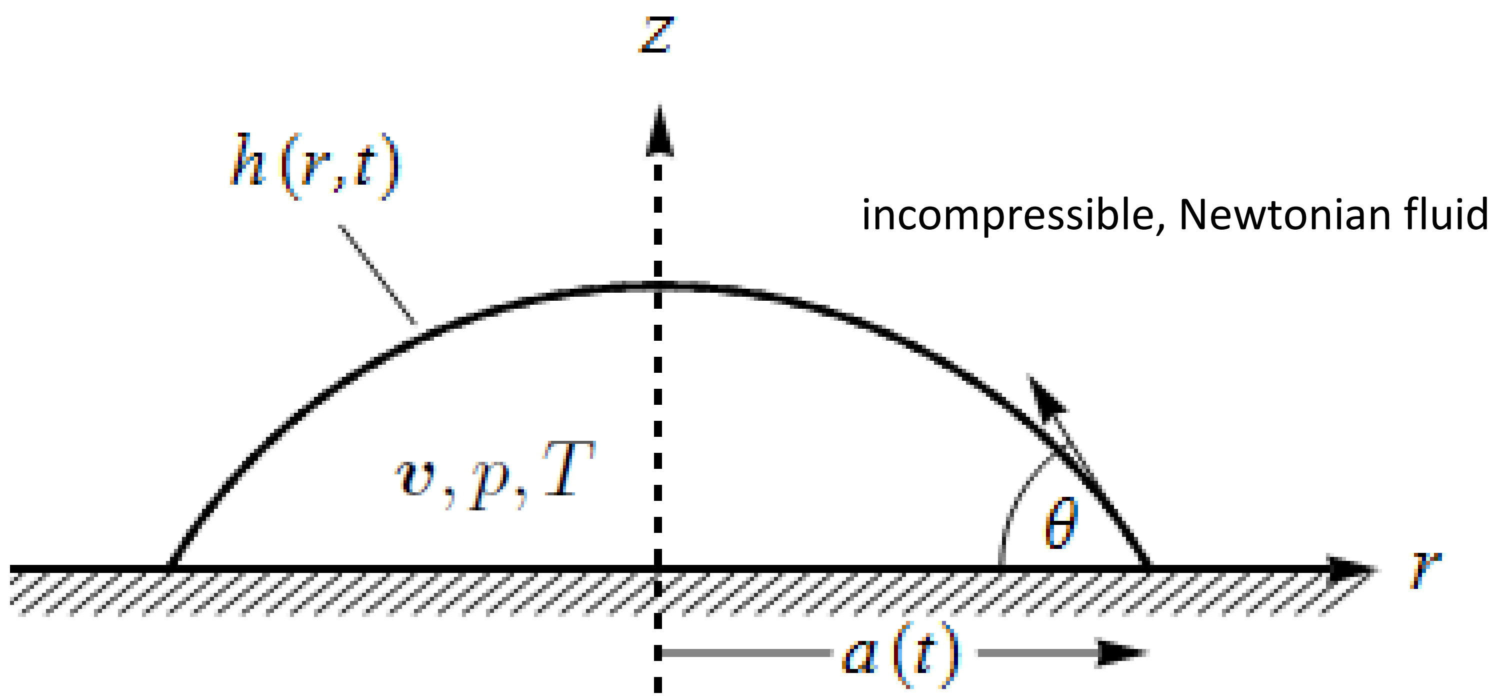
$$T_s(r) = T_0 - T_n(r)$$

choose applied temperature distribution

1) $T_n(r) = r$ 2) $T_n(r) = \ln r$

consistent with experiment

Solution method



v, p, T, h, a —— lubrication approximation ($a \gg h$) ——→ h, a —— quasi-static approximation ——→ a

Quasi-static spreading

steady droplet shape (small heating)

$$\left(h_{rr} + \frac{1}{r}h_r - Gh\right)_r + \Omega^2 r + \frac{3}{2}\frac{1}{h}\left(\hat{N}\,(T_n)_r + \hat{M}h_r\right) = 0.$$ “+ auxiliary conditions”

Bond

centrifugal

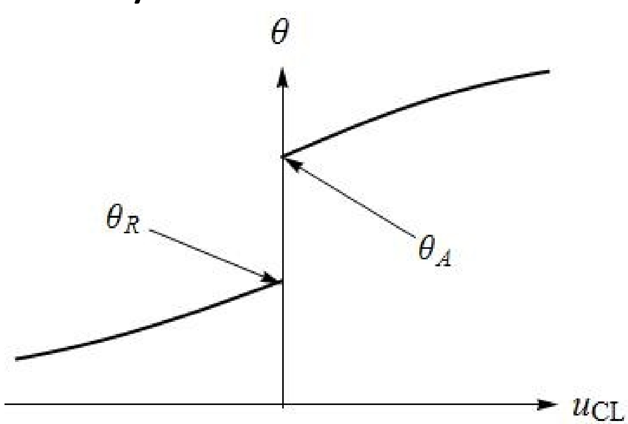
radial Marangoni

axial Marangoni

Imbalance of contact-line forces drive motion

$$F \sim (\theta - \theta_A)$$

Dynamic CL Law



response

$$\frac{da}{dt} = \left(\frac{\partial h}{\partial r} - \theta_A\right)^m$$

mobility exponent

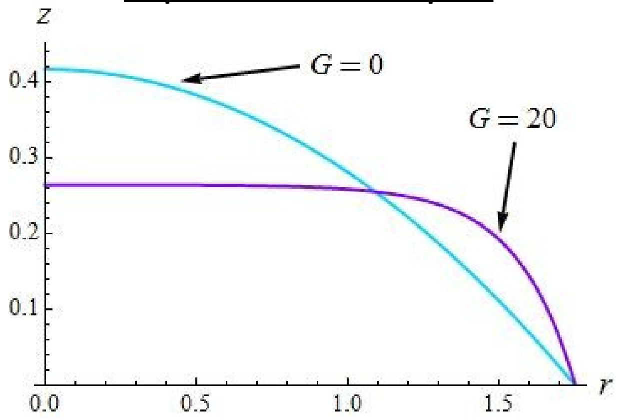
Map the problem to the contact line!

Outline of results

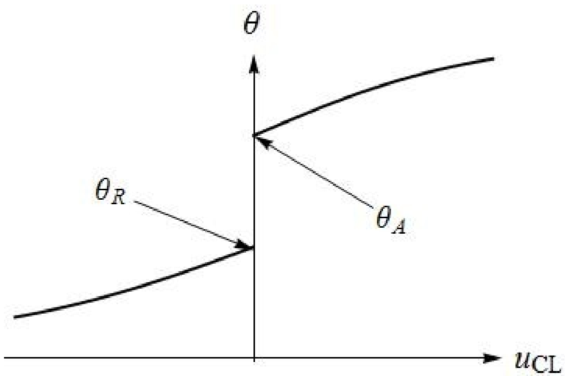
- large parameter space $(\hat{M}, \hat{N}, \Omega^2, G, \theta_A, m)$
  - equilibrium, flow fields and path to equilibrium
- review isothermal spreading
- linear temperature distribution
  - small heating
  - isorotational spreading
    - axial vs. radial thermal gradients
    - competition and bi-stability
  - centrifugal effects
- logarithmic temperature distribution
  - compare retraction laws to experiment

Isothermal spreading

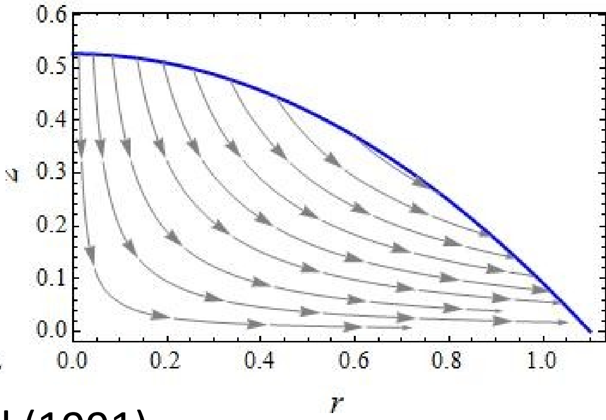
equilibrium shapes



spreading law



base flow



governing equation Ehrhard (1991)

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{G}{2\pi a}\frac{\mathcal{I}(\sqrt{G}a)}{\left(\sqrt{G}a - 2\mathcal{I}(\sqrt{G}a)\right)}$$

gravity dominant $G \rightarrow \infty$

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{\sqrt{G}}{2\pi}\frac{1}{a^2}$$

surface tension dominant $G \rightarrow 0$

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{4}{\pi a^3}$$

spreading laws

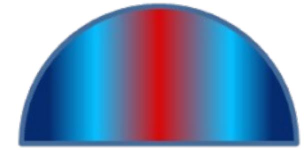
$$a(t) \sim t^{\frac{1}{2m+1}}$$

$$a(t) \sim t^{\frac{1}{3m+1}}$$

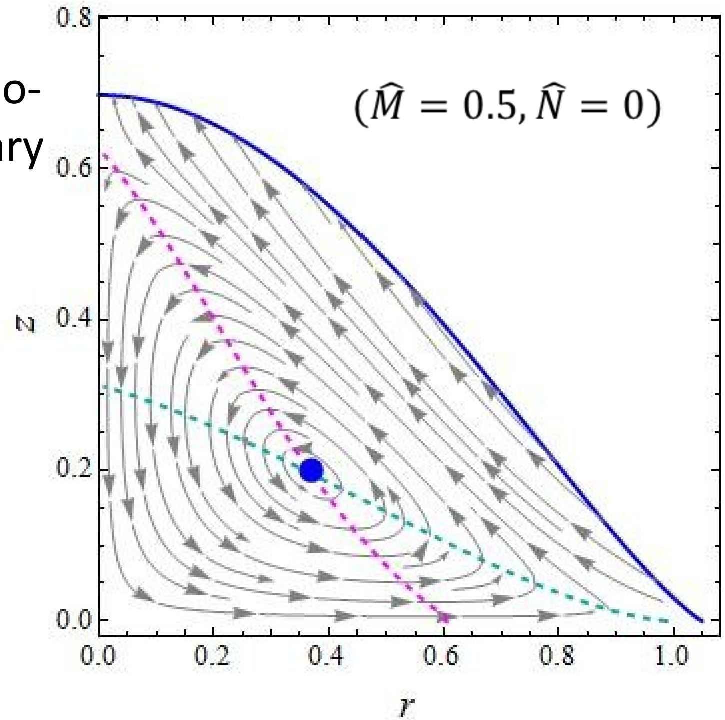
Tanner (1979), Chen (1988)

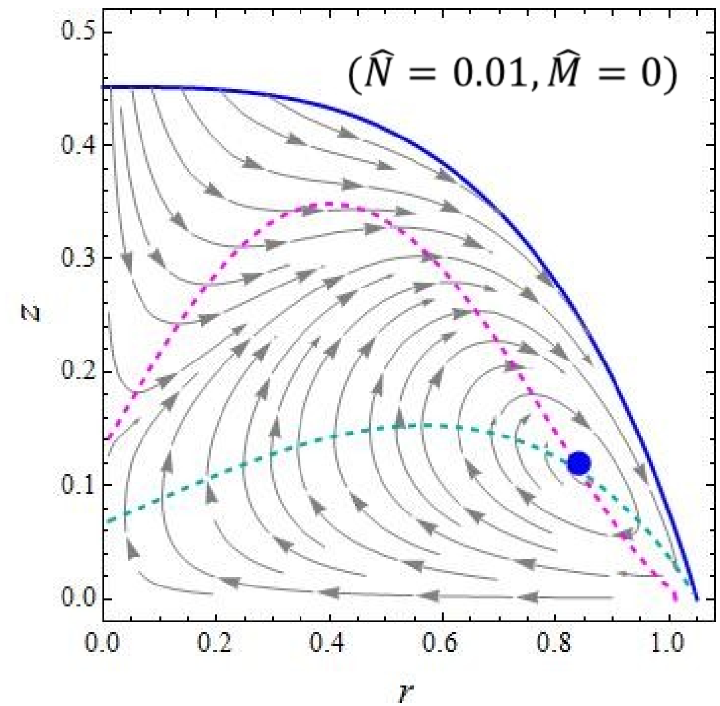
<u>axial gradient</u> vs. <u>radial gradient</u>

Ehrhard 91 (JFM) Smith 95 (JFM)—2D

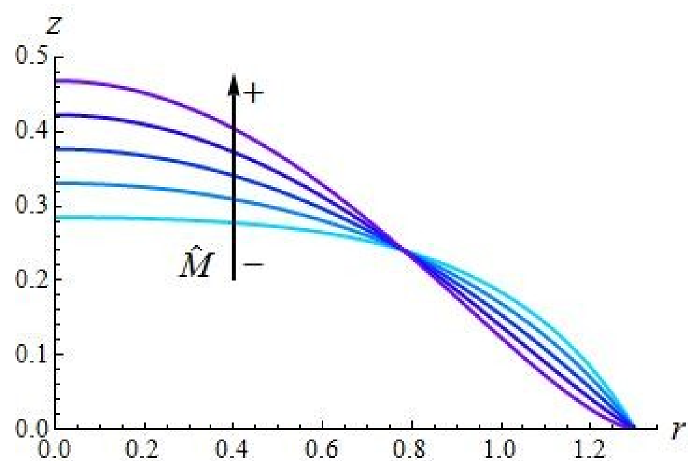


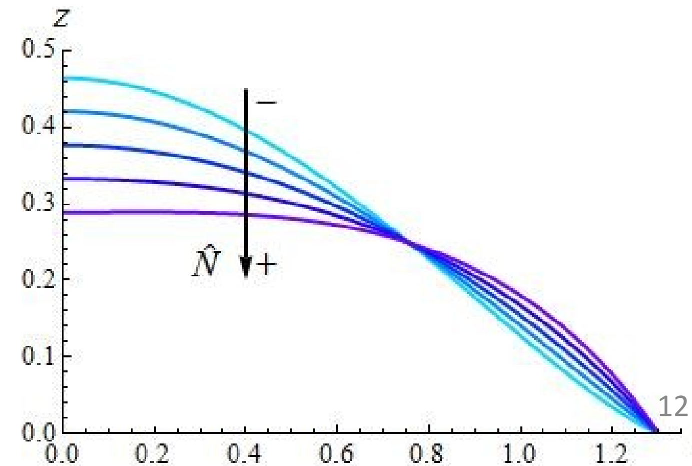
thermo-capillary flows





droplet shapes



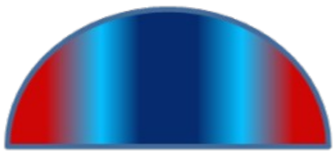


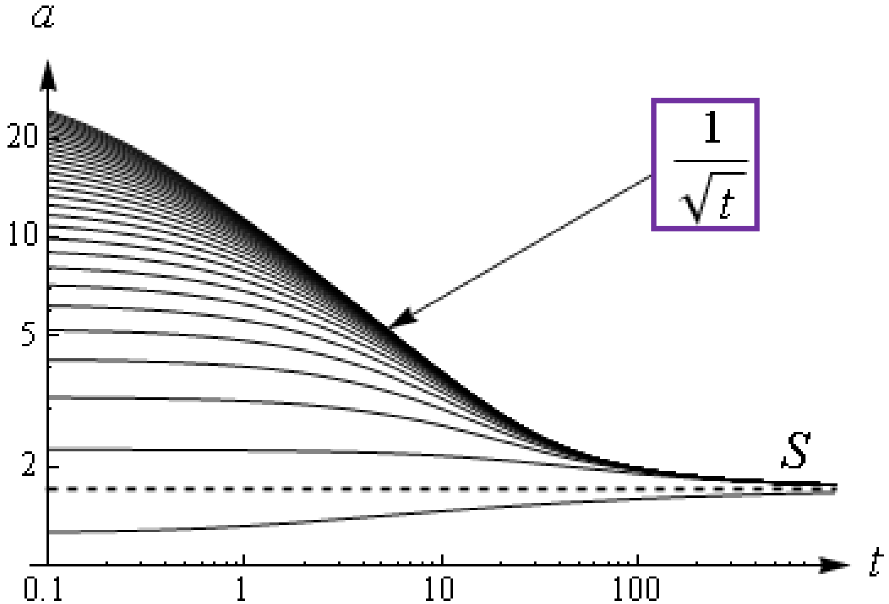
Approach to equilibrium

$$\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)^{1/3} + \theta_A = \frac{4}{\pi a^3} - \hat{M}\left(\frac{3}{8}\right)a + \hat{N}\left(\frac{\pi}{8}\right)a^4.$$

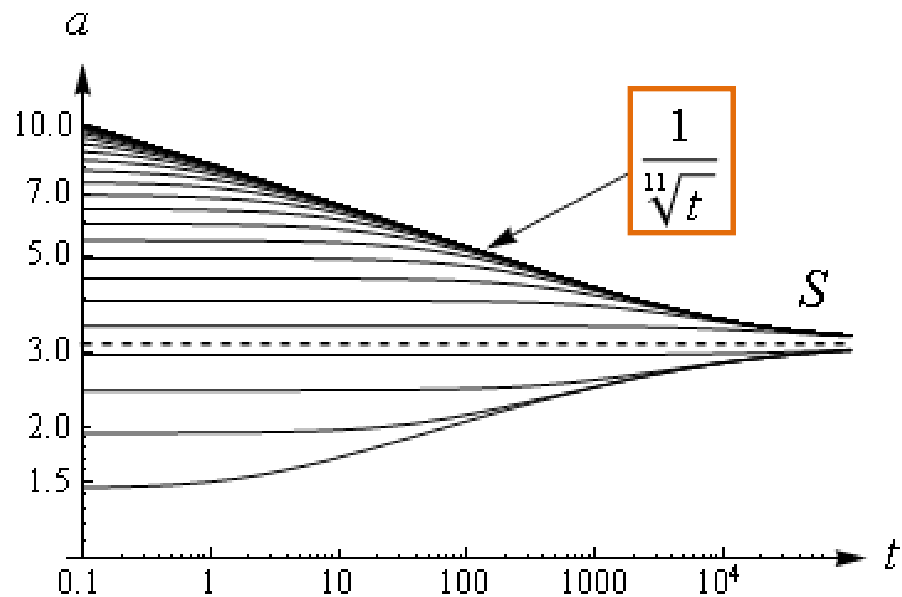
axial gradient

radial gradient



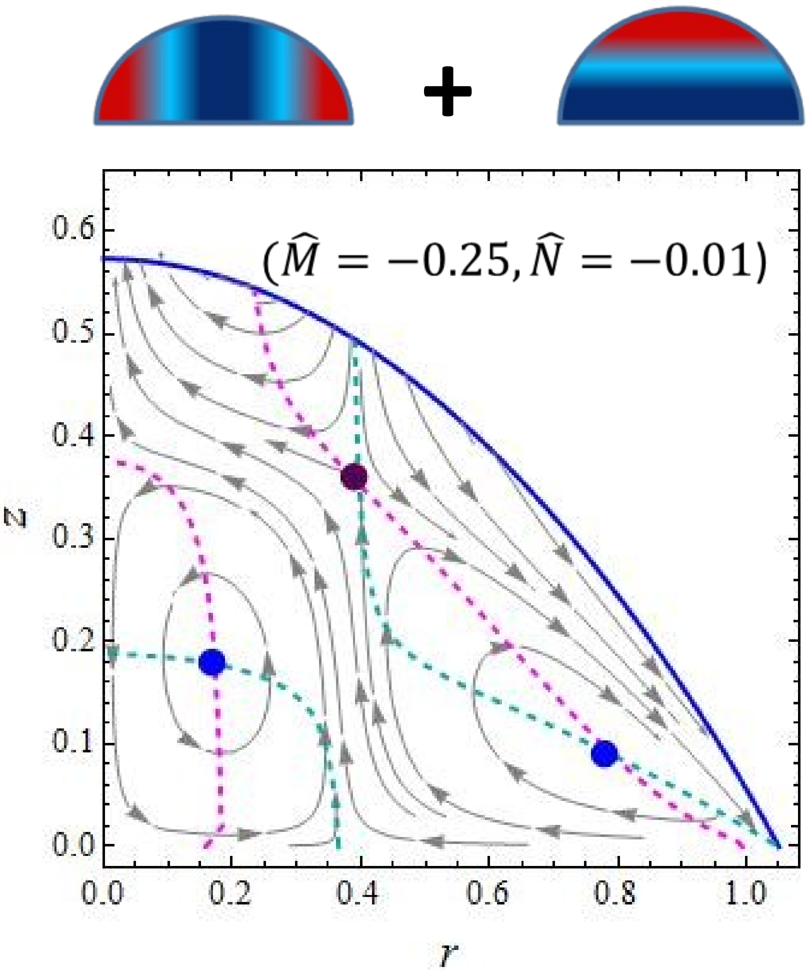


$(\widehat{M} = 0.5, \widehat{N} = 0)$

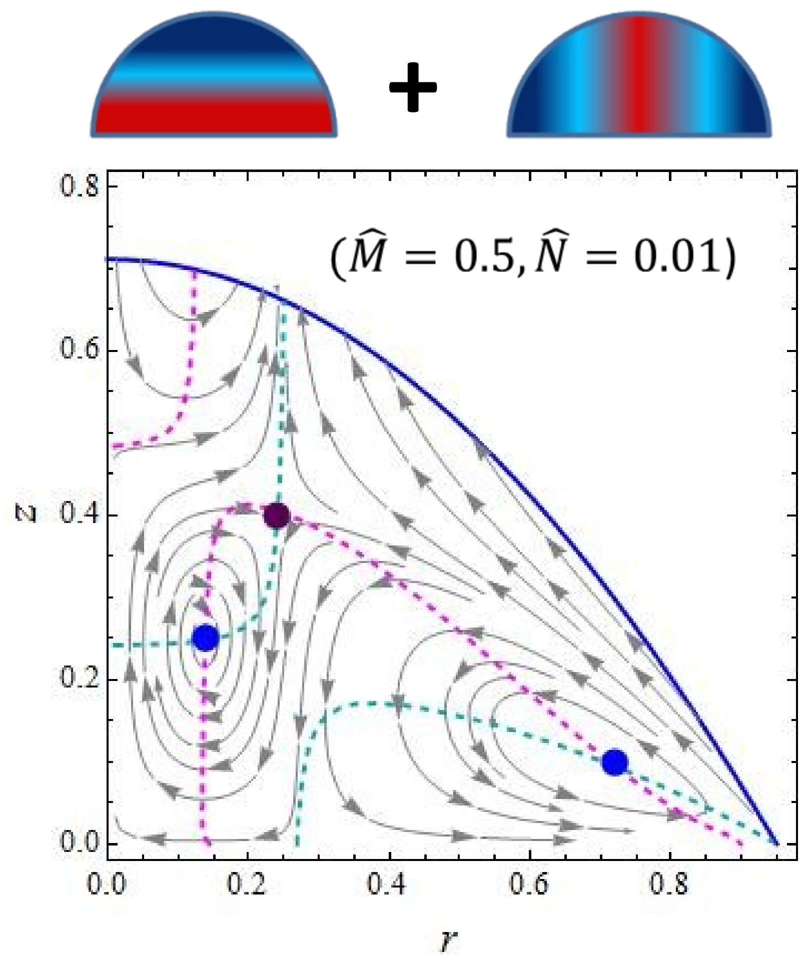


$(\widehat{N} = -0.01, \widehat{M} = 0)$

Competition



vs.



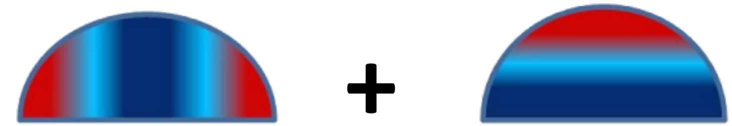
(1 or 3)

<u>equilibrium and Descartes' rule of signs</u>

$$\hat{N}\left(\frac{\pi}{8}\right)a^4 - \hat{M}\left(\frac{3}{8}\right)a - \theta_A + \frac{4}{\pi a^3} = 0$$

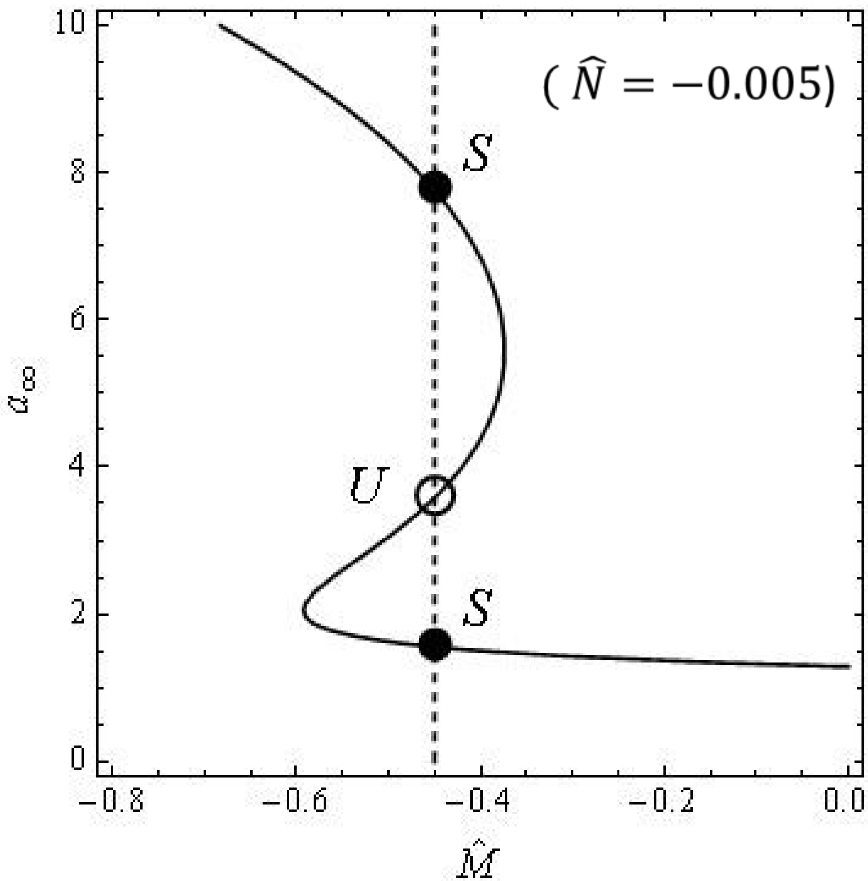
(0 or 2)

Bi-stability

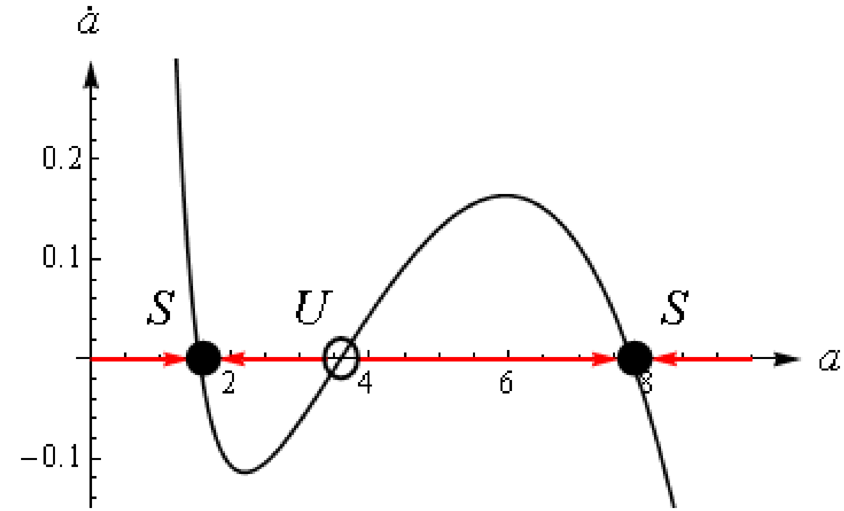


$$\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)^{1/3} + \theta_A = \frac{4}{\pi a^3} - \hat{M}\left(\frac{3}{8}\right)a + \hat{N}\left(\frac{\pi}{8}\right)a^4$$

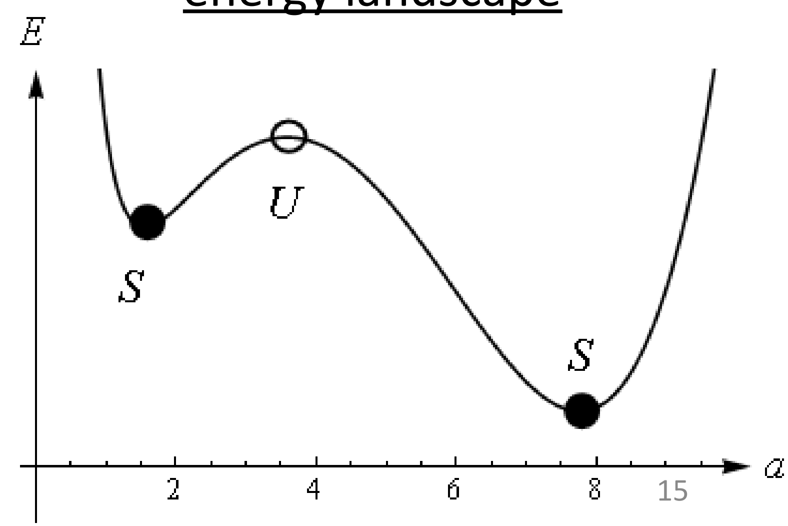
bifurcation diagram



force balance

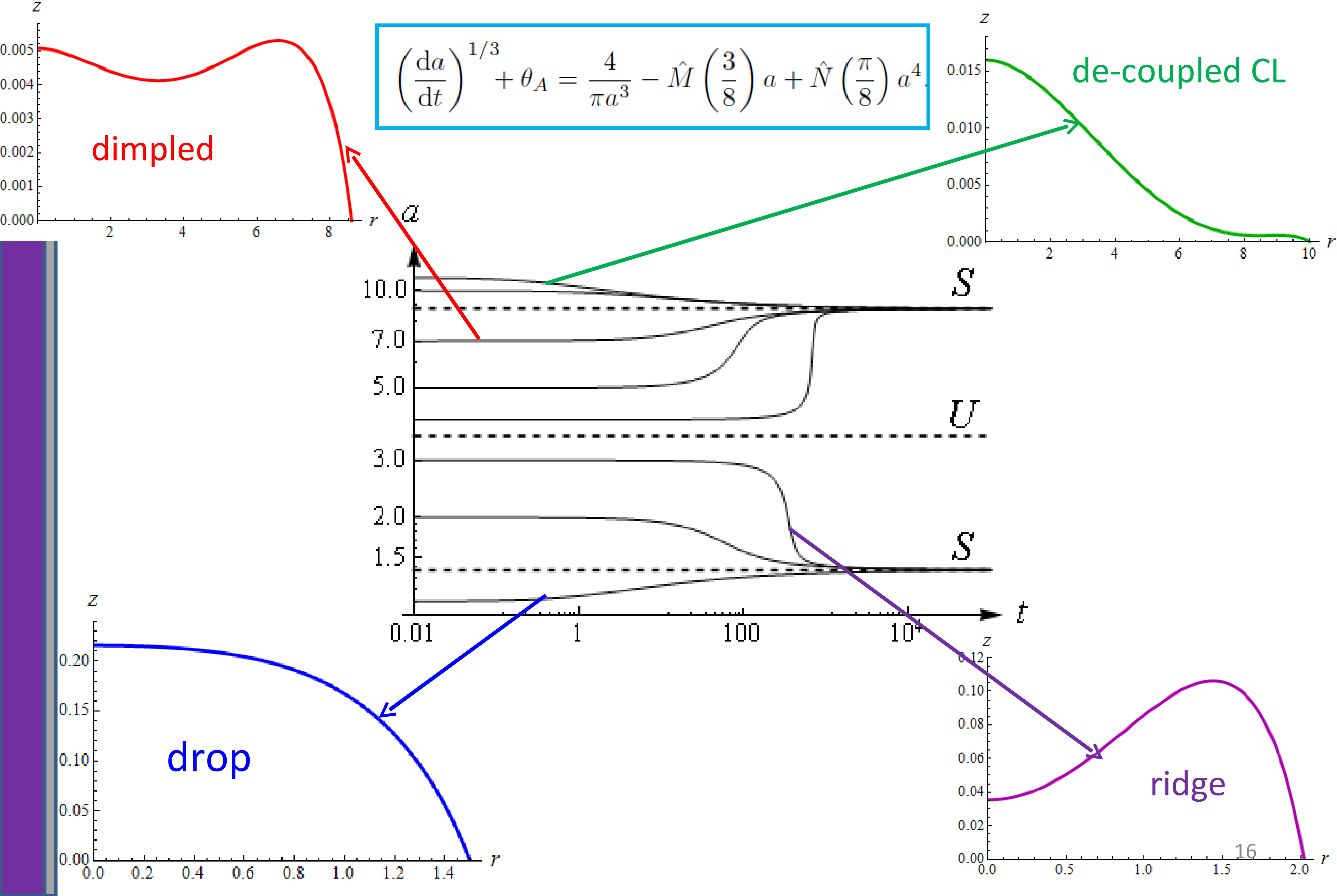


energy landscape



Approach to equilibrium

$$\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)^{1/3} + \theta_A = \frac{4}{\pi a^3} - \hat{M}\left(\frac{3}{8}\right)a + \hat{N}\left(\frac{\pi}{8}\right)a^4$$



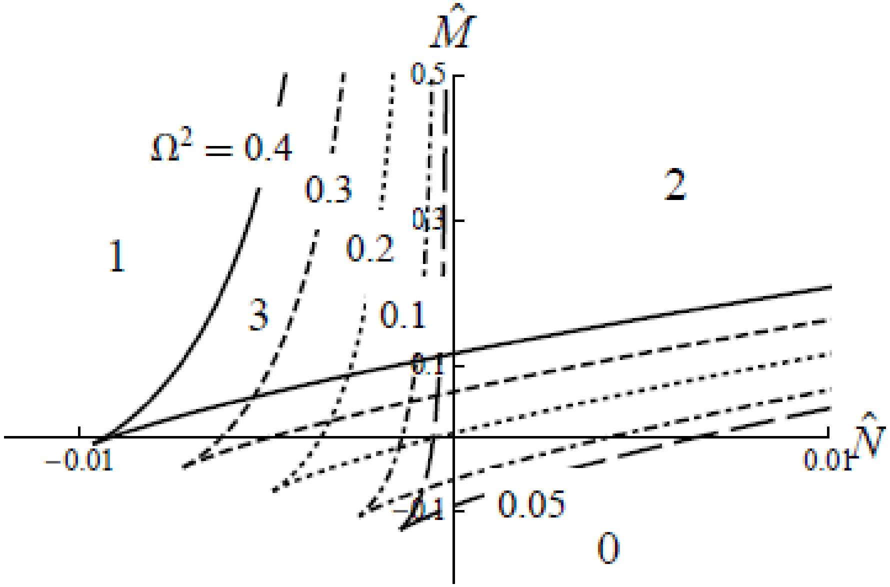
Centrifugal effects

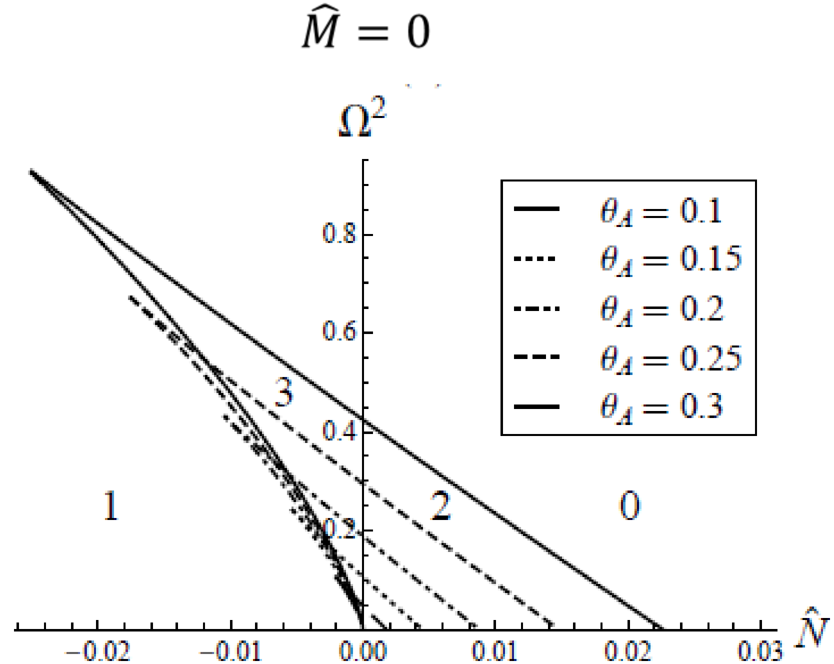
<u>equilibrium equation</u>

$$\hat{N}\left(\frac{\pi}{8}\right)a^4 + \Omega^2\left(\frac{1}{24}\right)a^3 - \hat{M}\left(\frac{3}{8}\right)a - \theta_A + \frac{4}{\pi a^3} = 0$$

centrifugal forces can replace/overcome the effect of heat transfer!

<u>`slices' of parameter space</u>





Logarithmic temperature profile

$$(T_n)_r = \frac{1}{r} \longrightarrow \boxed{\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)^{1/m} + \theta_A = \frac{4}{\pi a^3} - \hat{M}\left(\frac{3}{8}\right)a + C_{\hat{N}\Omega}a^3}$$

equilibrium equation

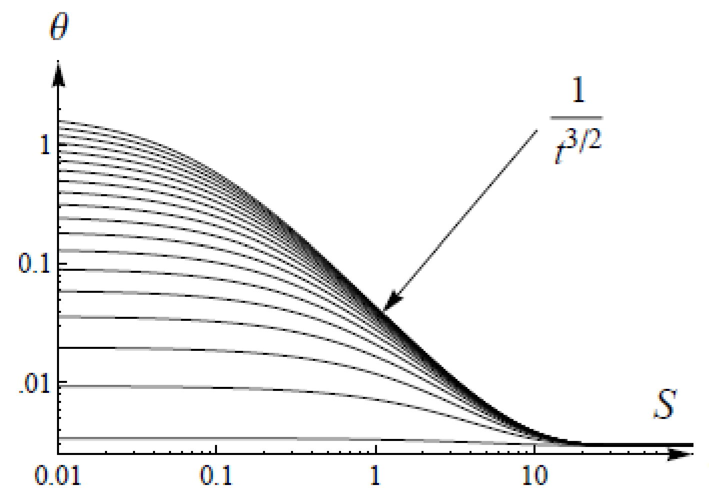
lumped parameter

$$C_{\hat{N}\Omega}a^3 - \hat{M}\left(\frac{3}{8}\right)a + \frac{4}{\pi a^3} - \theta_A = 0 \quad \text{with} \quad C_{\hat{N}\Omega} \equiv \frac{\Omega^2}{24} + \hat{N}\left(\frac{3\pi}{16}\right)$$

⟶ heat transfer is necessary to achieve bi-stability

retraction rates are consistent with Mukhopadhyay & Behringer 2009

$$\Omega^2 = 0, \widehat{M} = 0,\ \theta_A = 0, m = 1$$



Concluding remarks

- bi-stability <---> competition
- centrifugal forces can enlarge regions of bi-stability
  - thermal conditions may be relaxed
  - more control
- map regions of indefinite spreading
- generalized to other heating conditions

Acknowledgement: NSF FRG Grant # DMS-0968258

Michael Shearer, Karen Daniels, Joshua Dijksman

Quasi-static spreading $(C \to 0)$

steady droplet shape (small heating)

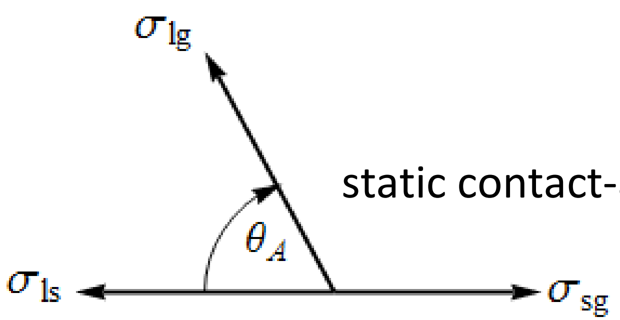
$$\left(h_{rr} + \frac{1}{r}h_r - Gh\right)_r + \Omega^2 r + \frac{3}{2}\frac{1}{h}\left(\hat{N}\left(T_n\right)_r + \hat{M}h_r\right) = 0.$$ "+ auxiliary conditions"

Imbalance of contact-line forces drive motion

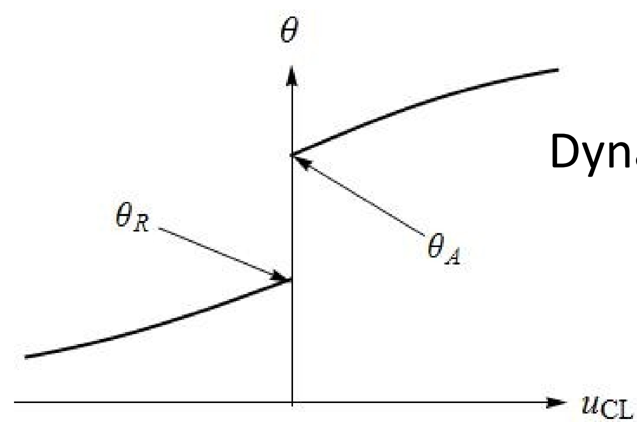
$F \sim (\theta - \theta_A)$ → response →

$$\frac{da}{dt} = \left(\frac{\partial h}{\partial r} - \theta_A\right)^m$$

← mobility exponent



static contact-angle



Dynamic CL Law

Map the problem to the contact line!

Evolution equation

$$C h_t + \frac{1}{r}\left[r\left(\left(h_{rr} + \frac{1}{r}h_r - Gh\right)_r + \Omega^2 r\right)\left(\frac{1}{3}h^3 + \beta h^2\right) + r\frac{C}{\Delta C}\left(N\frac{(T_n)_r}{1+Bh} + B\frac{h_r(1-NT_n)}{(1+Bh)^2}\right)\left(\frac{1}{2}h^2 + \beta h\right)\right]_r = 0$$

<u>auxiliary conditions</u>

$$h_r = h_{rrr} = 0\Big|_{r=0}$$

$$h(a(t),t) = 0$$

$$\frac{\partial h}{\partial r}(a(t),t) = -\theta(t)$$

$$2\pi\int_0^{a(t)} r h(r,t)\mathrm{d}r = 1$$

$$\frac{da}{dt} = (\theta(t) - \theta_A)^m$$

scale with σ
(surface tension)

<u>dimensionless numbers</u>

C	capillary
G	Bond
Ω^2	centrifugal
B	Biot (heat transfer)
N	thermal gradient
ΔC	thermocapillary
β	slip length

Evolution equation

$$Ch_t + \frac{1}{r}\left[r\left(\left(h_{rr} + \frac{1}{r}h_r - Gh\right)_r + \Omega^2 r\right)\left(\frac{1}{3}h^3 + \beta h^2\right) + r\frac{C}{\Delta C}\left(N\frac{(T_n)_r}{1+Bh} + B\frac{h_r\left(1 - N\,T_n\right)}{(1+Bh)^2}\right)\left(\frac{1}{2}h^2 + \beta h\right)\right]_r = 0$$

<u>auxiliary conditions</u>

$$h_r = h_{rrr} = 0\Big|_{r=0}$$

$$h(a(t),t) = 0$$

$$\frac{\partial h}{\partial r}(a(t),t) = -\theta(t)$$

$$2\pi\int_0^{a(t)} rh(r,t)\mathrm{d}r = 1$$

$$\frac{da}{dt} = (\theta(t) - \theta_A)^m$$

<u>dimensionless numbers</u>

$C = \dfrac{\mu\kappa\theta_0^{m-3}}{\sigma_0}$ Capillary

$G = \dfrac{\rho g a_0^2}{\sigma_0}$ Bond

$\Omega^2 = \dfrac{\rho\omega^2 a_0^3\theta_0^{2-m}}{\mu\kappa}$ Centrifugal

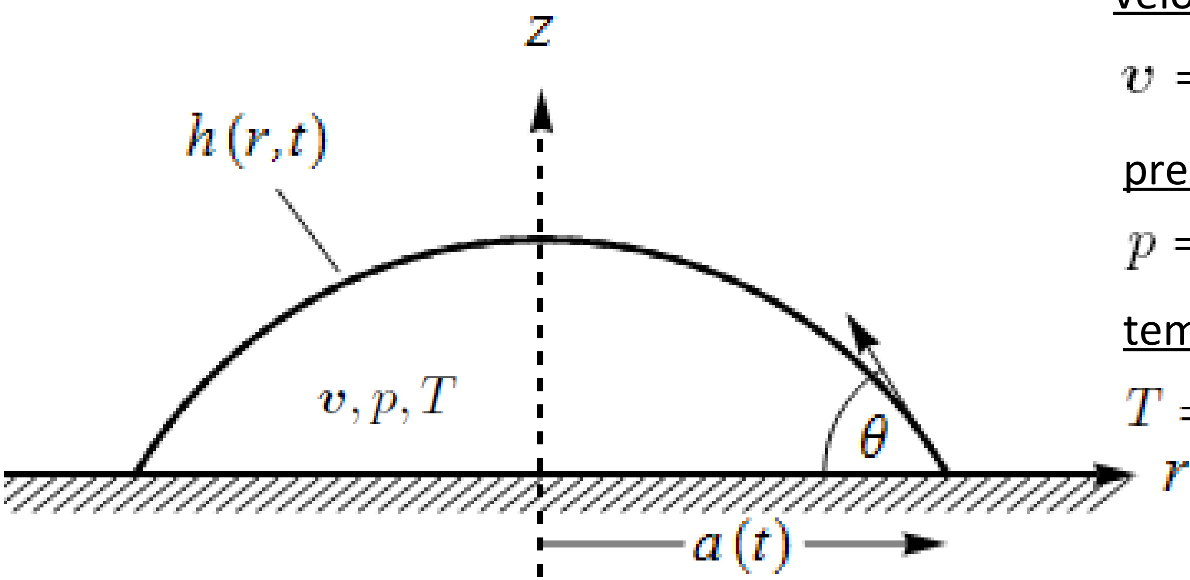
$\beta = \dfrac{\beta'}{a_0\theta_0}$ Slip length

$\Delta C = \dfrac{\mu\kappa\theta_0^{m-1}}{\gamma\left(T_0 - T_\infty\right)}$ Thermocapillary

$B = \dfrac{h_g a_0\theta_0}{k}$ Biot

$N = \dfrac{b a_0}{T_0 - T_\infty}$ Thermal gradient

Field equations



velocity field

$$v = u_r(r,z)\hat{r} + u_z(r,z)\hat{z}$$

pressure

$$p = p(r,z)$$

temperature

$$T = T(r,z)$$

incompressibility

$$\nabla \cdot v = 0$$

Stokes flow

$$\mu\nabla^2 v - \nabla p - \rho g\hat{z} + \rho\omega^2 r\hat{r} = 0$$

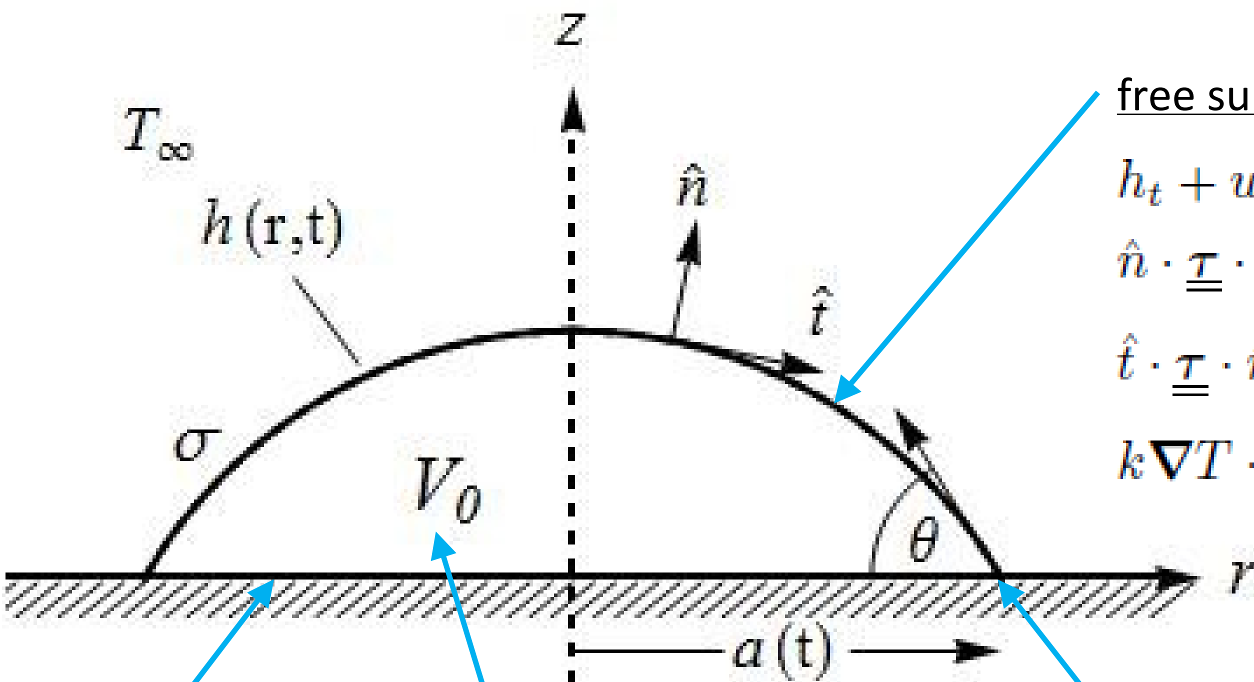
energy balance

$$\rho c_p (T_t + v \cdot \nabla T) = k\nabla^2 T$$

surface tension relationship

$$\sigma = \sigma_0 - \gamma(T - T_0)$$

Boundary conditions



free surface

$$h_t + u_r h_r = u_z$$

$$\hat{n} \cdot \underline{\underline{\tau}} \cdot \hat{n} = -\sigma\,(2H)$$

$$\hat{t} \cdot \underline{\underline{\tau}} \cdot \hat{n} = \hat{t} \cdot \boldsymbol{\nabla}\sigma$$

$$k\boldsymbol{\nabla}T \cdot \hat{n} = -h_g\,(T - T_\infty)$$

substrate

$$u_z = 0,$$

$$u_r = \beta'\,(u_r)_z,$$

$$T = T_s\,(r) = T_0 + T_n(r)$$

volume

$$2\pi \int_0^{a(t)} r h(r,t)\mathrm{d}r = V_0$$

contact-line

$$h(a(t),t) = 0$$

$$\frac{\partial h}{\partial r}(a(t),t) = -\tan\theta(t)$$

$$\frac{da}{dt} = \kappa\,(\theta - \theta_A)^m$$

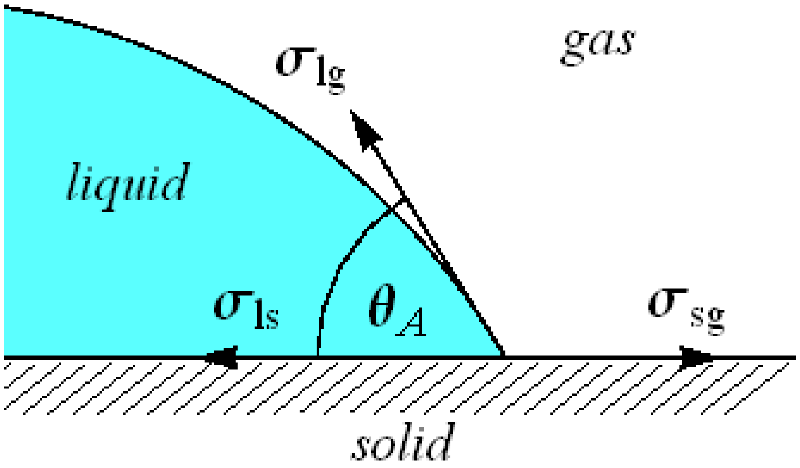
Wetting

modeling microscopic effects using macroscopic quantities

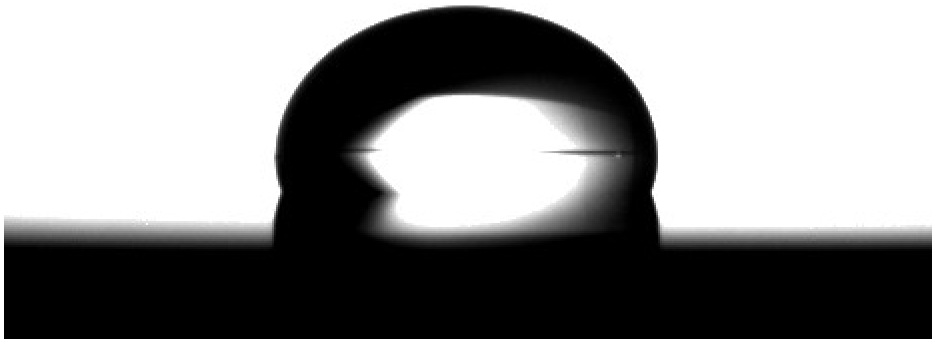
Young-Dupre equation:

$$\sigma_{sg} - \sigma_{ls} \equiv \sigma_{lg} \cos\theta_A$$

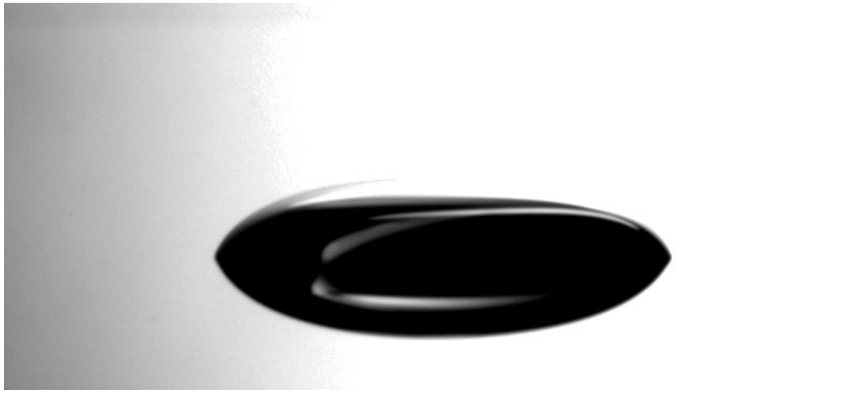
force balance (statics)



non-wetting ($\theta_s > 90^\circ$)



wetting ($\theta_A < 90^\circ$)



Evolution equation

$$Ch_t + \frac{1}{r}\left[r\left(\left(h_{rr} + \frac{1}{r}h_r - Gh\right)_r + \Omega^2 r\right)\left(\frac{1}{3}h^3 + \beta h^2\right) + r\frac{C}{\Delta C}\left(\frac{N}{1+Bh} + B\frac{h_r(1-Nr)}{(1+Bh)^2}\right)\left(\frac{1}{2}h^2 + \beta h\right)\right]_r = 0$$

<u>auxiliary conditions</u>

$$h_r = h_{rrr} = 0\Big|_{r=0}$$

$$h(a(t),t) = 0$$

$$\frac{\partial h}{\partial r}(a(t),t) = -\theta(t)$$

$$2\pi\int_0^{a(t)} rh(r,t)\mathrm{d}r = 1$$

$$\frac{da}{dt} = (\theta(t) - \theta_A)^m$$

<u>dimensionless numbers</u>

$C = \dfrac{\mu\kappa\theta_0^{m-3}}{\sigma_0}$ Capillary

$G = \dfrac{\rho g a_0^2}{\sigma_0}$ Bond

$\Omega^2 = \dfrac{\rho\omega^2 a_0^3\theta_0^{2-m}}{\mu\kappa}$ Centrifugal

$\beta = \dfrac{\beta'}{a_0\theta_0}$ Slip length

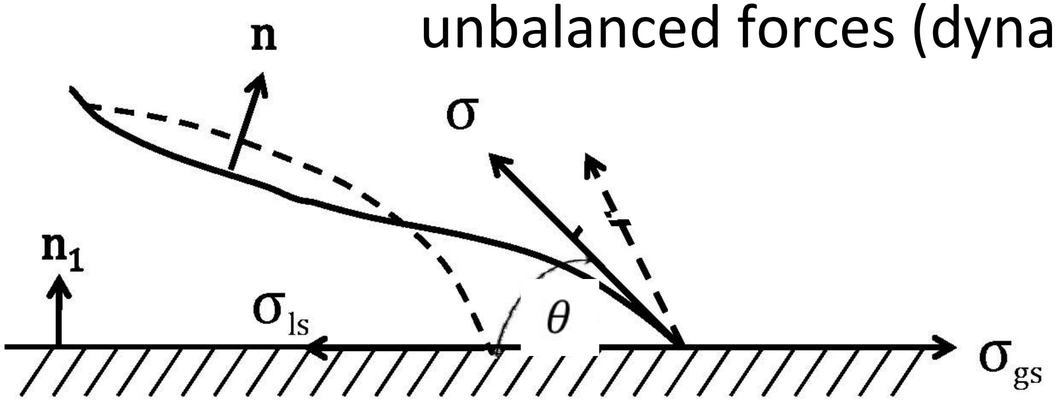
$\Delta C = \dfrac{\mu\kappa\theta_0^{m-1}}{\gamma(T_0 - T_\infty)}$ Thermo-capillary

$B = \dfrac{h_g a_0\theta_0}{k}$ Biot

$N = \dfrac{b a_0}{T_0 - T_\infty}$ Thermal gradient

Spreading

unbalanced forces (dynamics)

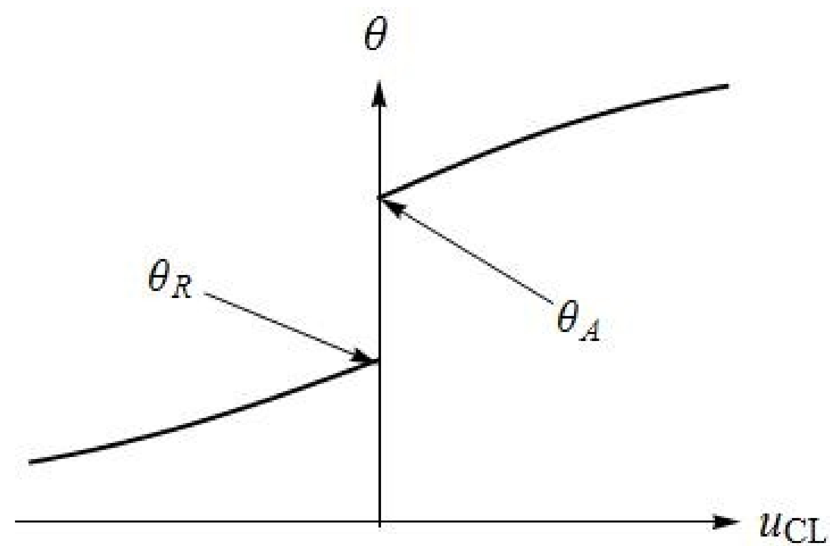


Spreading law

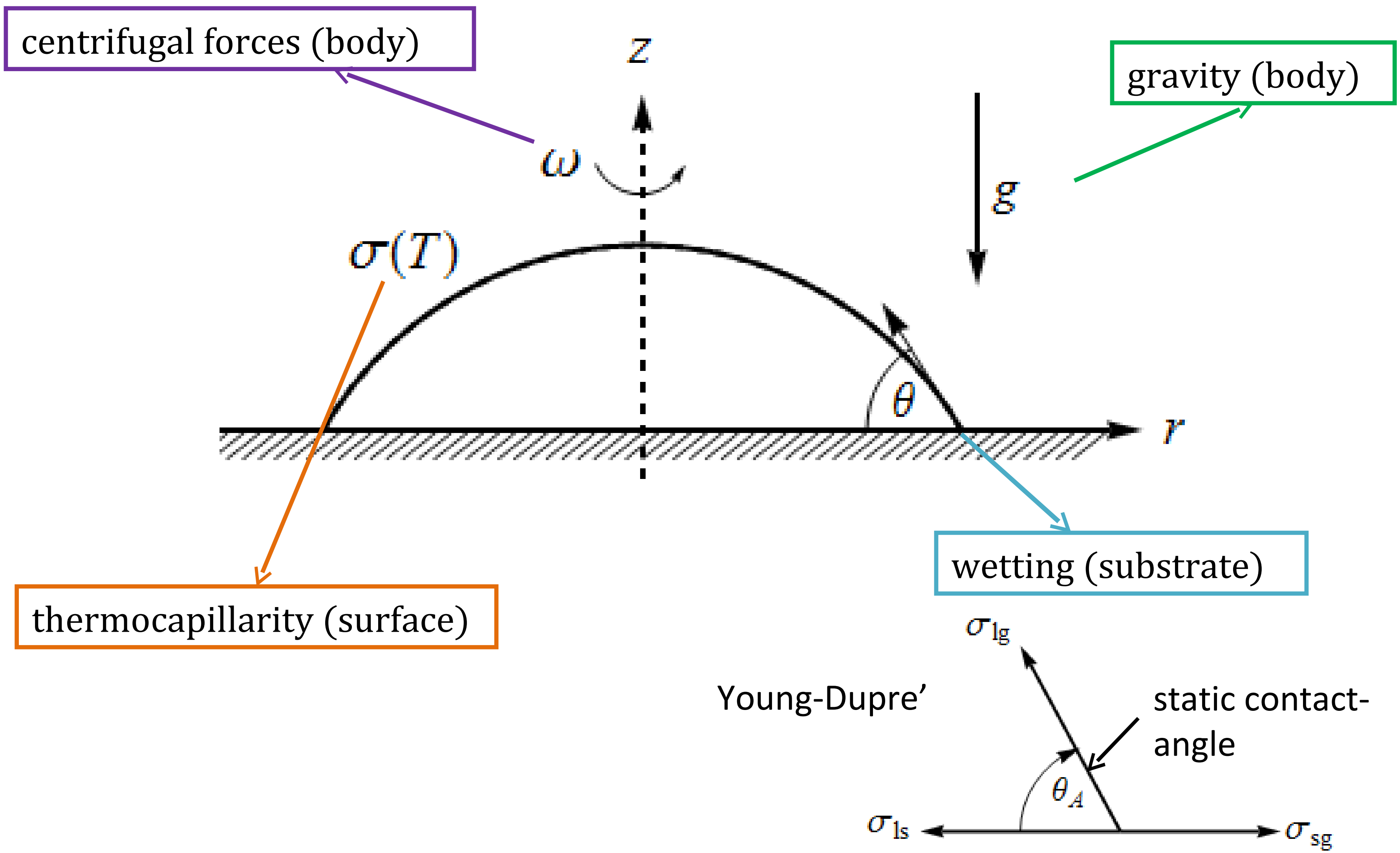
spreading

$$u_{CL} = (\theta - \theta_A)^m$$

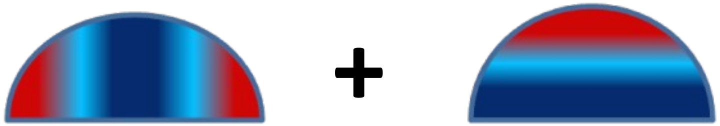
wetting (advancing contact angle)

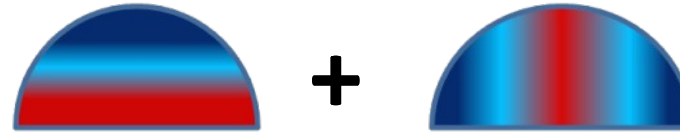


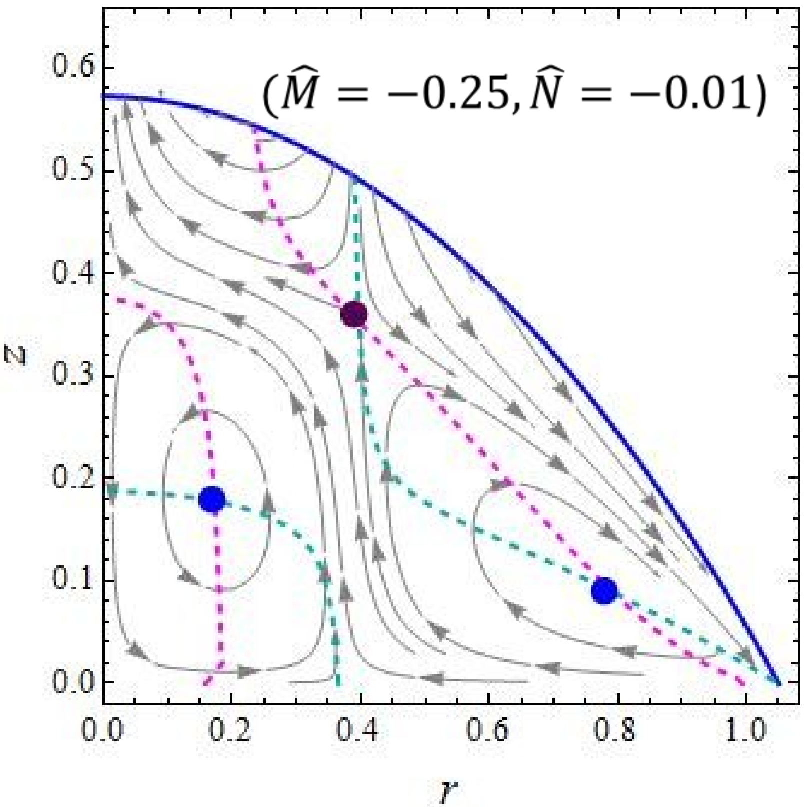
Why do fluids spread?



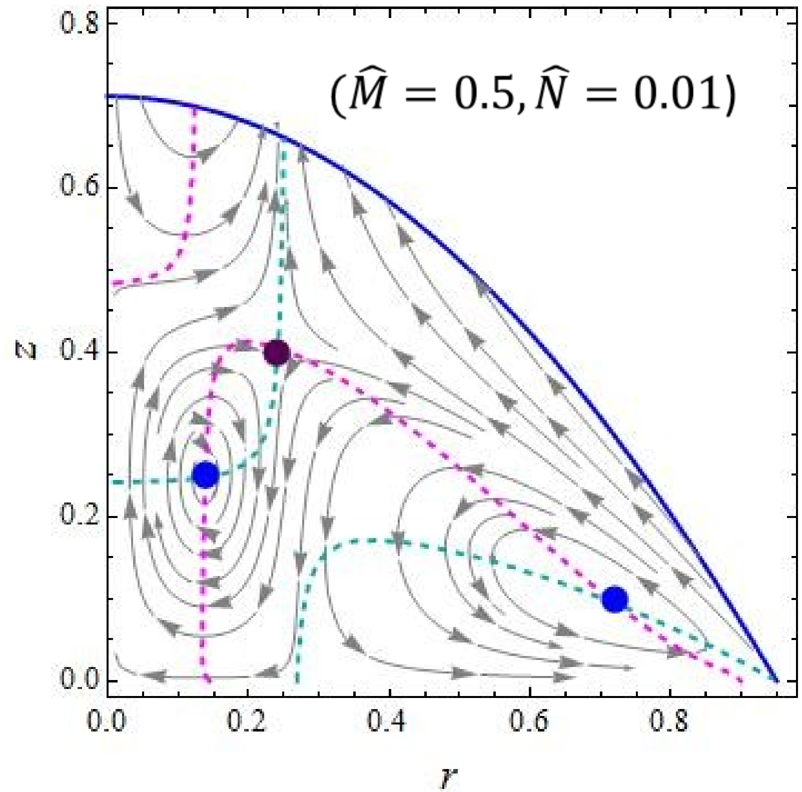
Competition

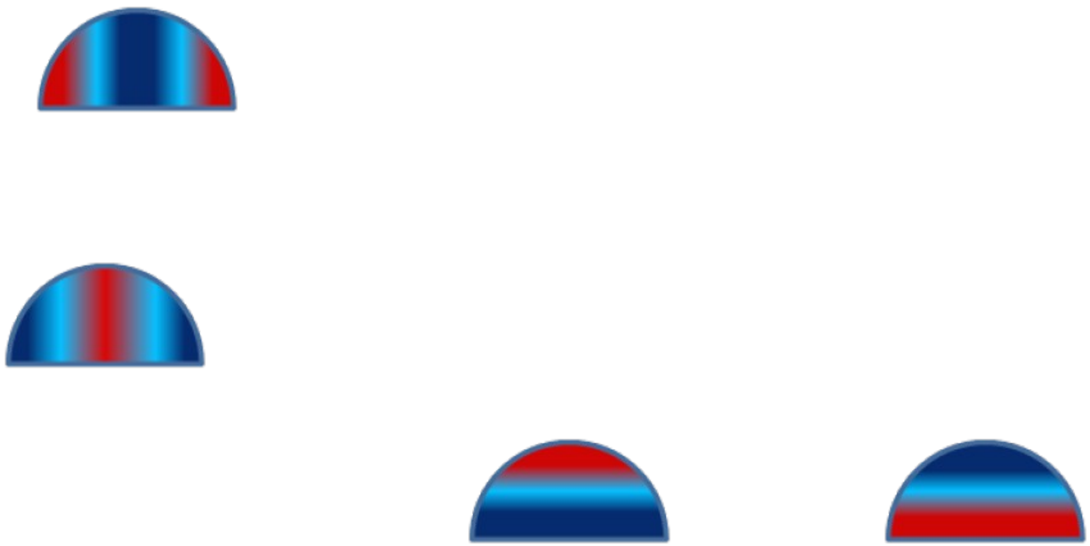






vs.



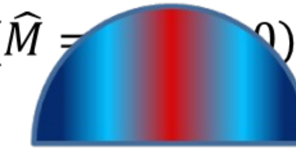


axial gradient ($\hat{N}$ = ...)

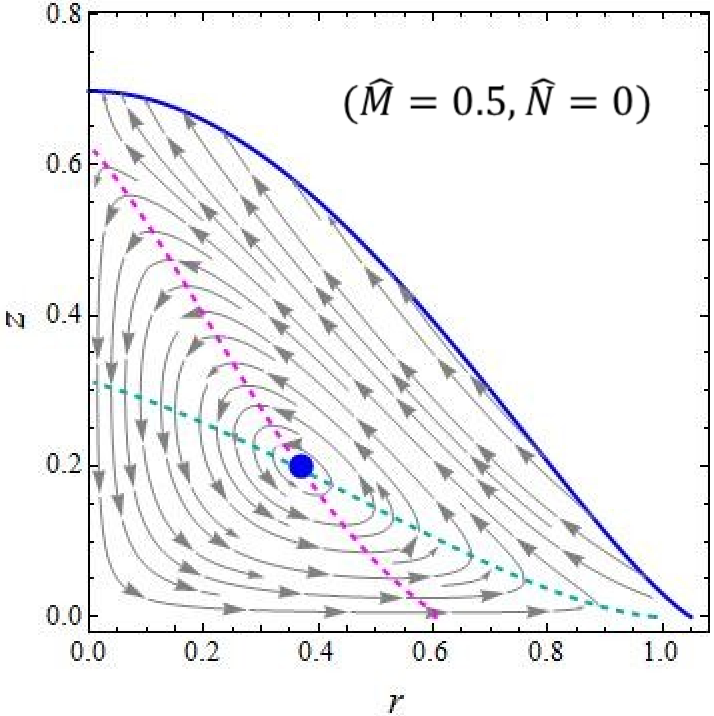
Ehrhard 91 (JFM)

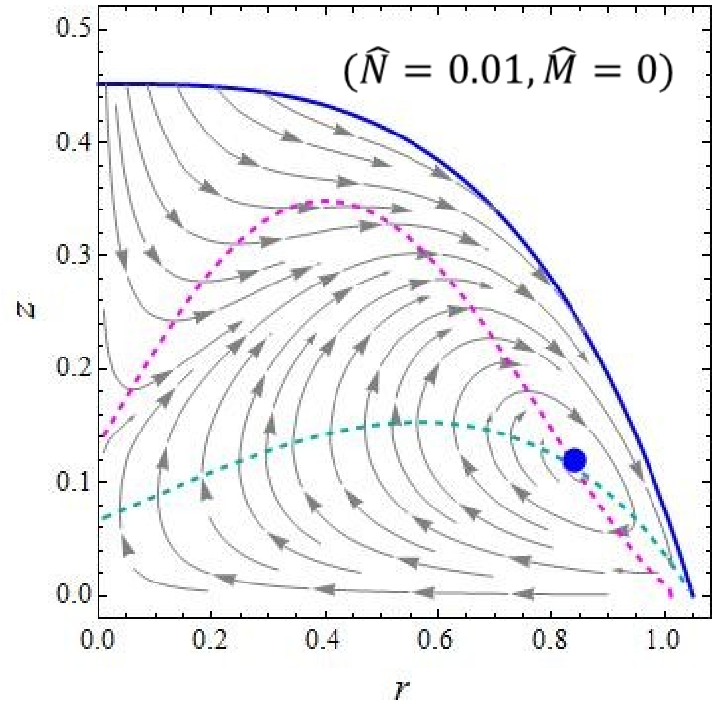
radial gradient ($\hat{M}$ = ...)

Smith 95 (JFM)—2D

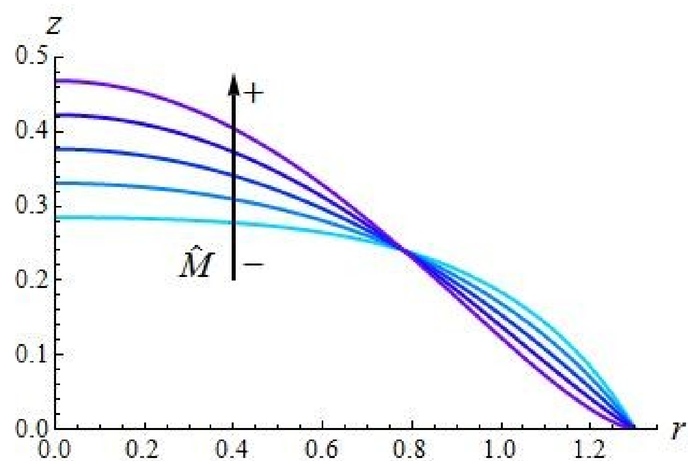


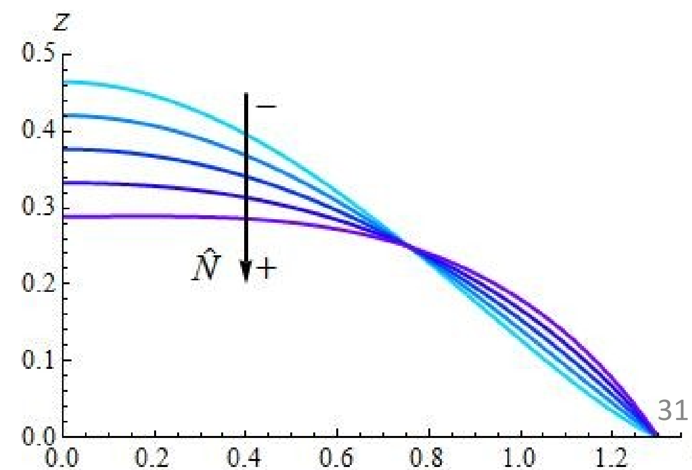
flows





shapes





Quasi-static spreading

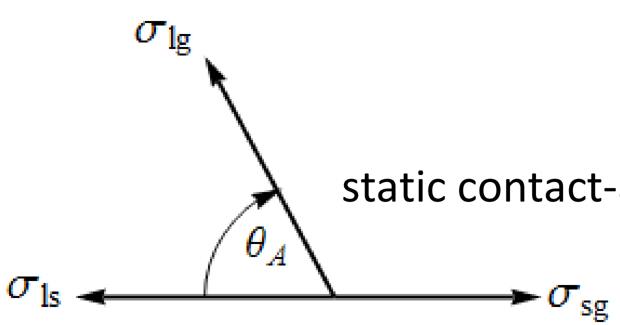
<u>steady droplet shape</u>

$$\left(h_{rr} + \frac{1}{r}h_r\right)_r + \frac{3}{2}\frac{1}{h}\left(\hat{N}\left(T_n\right)_r + \hat{M}h_r\right) = 0$$

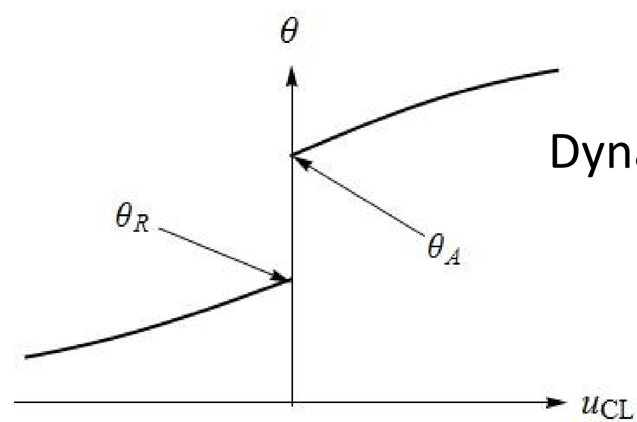
"+ auxiliary conditions"

<u>Imbalance of contact-line forces drive motion</u>

$F \sim (\theta - \theta_A)$ → response → $\frac{da}{dt} = \kappa\left(\theta - \theta_A\right)^m$ ← mobility exponent



static contact-angle



Dynamic CL Law

<u>applied temperature gradient</u>

$$T_n = r$$

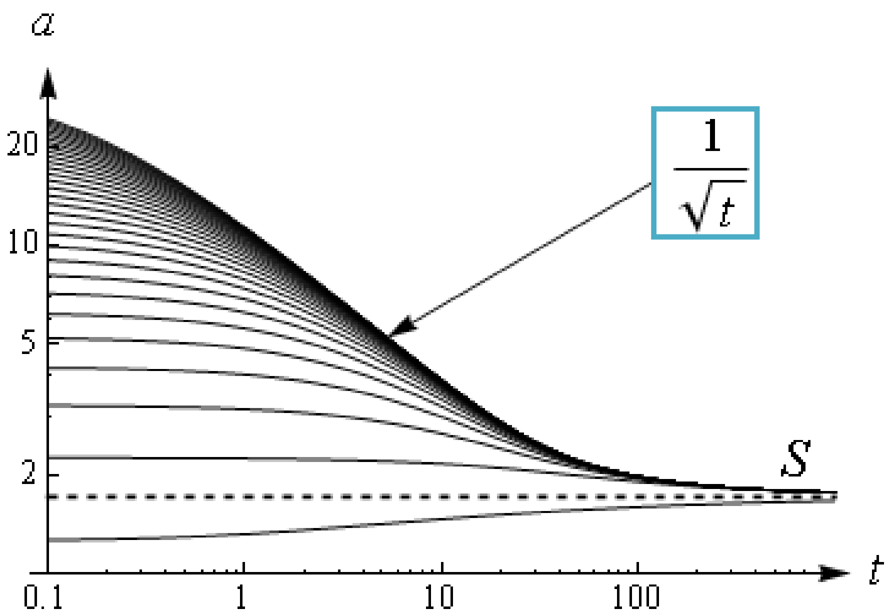
Map the problem to the contact line!

Approach to equilibrium

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{4}{\pi a^3} - \hat{M}\left(\frac{3}{8}a\right) + \hat{N}\left(\frac{\pi}{8}a^4\right)$$

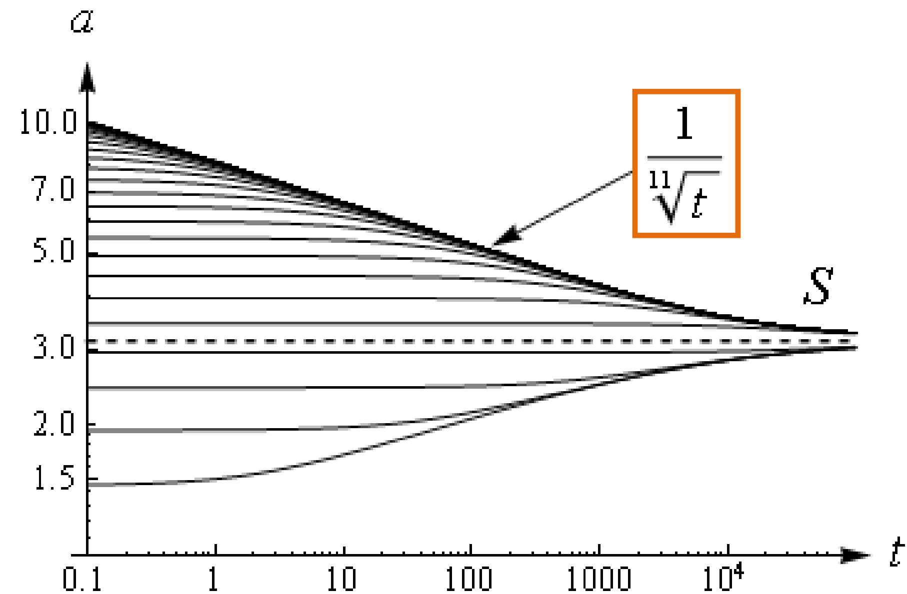
axial gradient

$\widehat{M} = 0.5, \widehat{N} = 0$



radial gradient

$\widehat{N} = -0.01, \widehat{M} = 0$

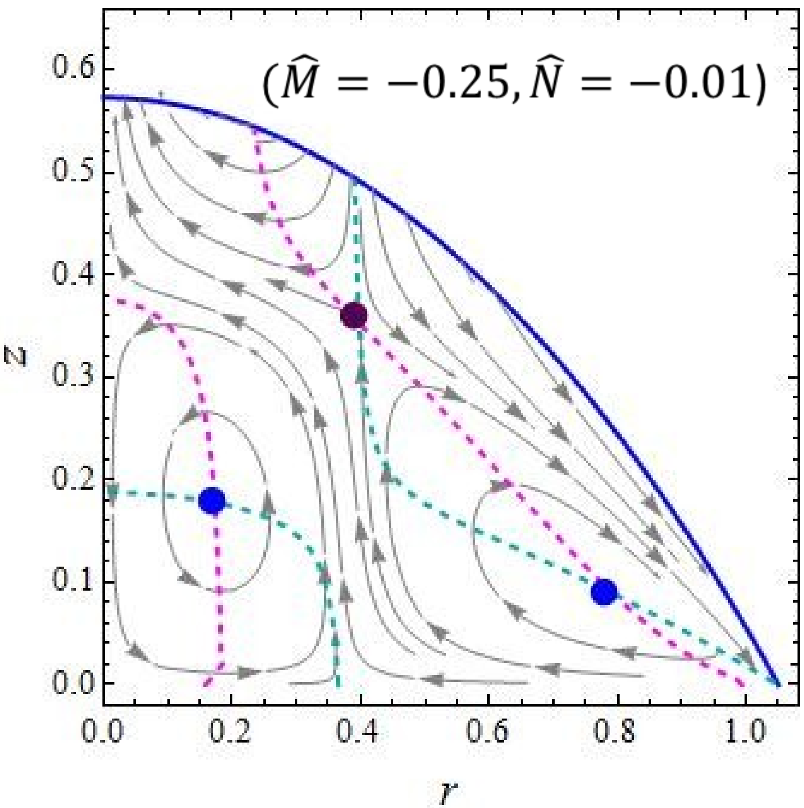


$m = 3$

mobility exponent

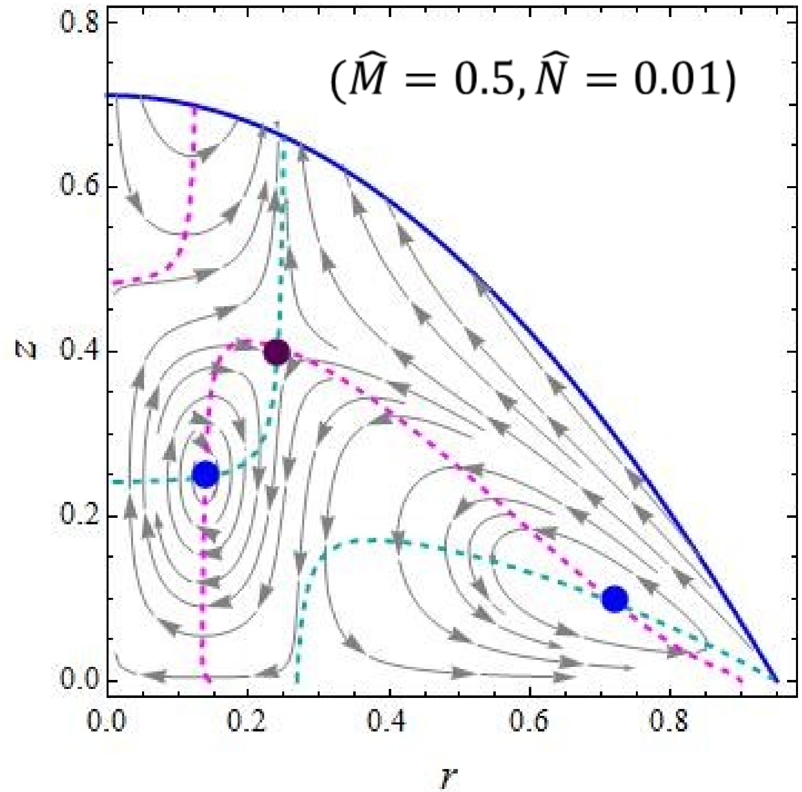
Competition

axial-cool, radial-in



vs.

axial-heat, radial-out

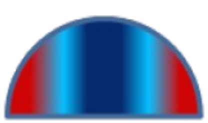


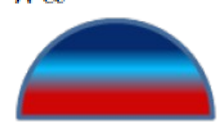
(1 or 3)

<u>equilibrium and Descartes' rule of signs</u>

(0 or 2)

$$\hat{N}\left(\frac{\pi}{8}\right)a^4 - \hat{M}\left(\frac{3}{8}\right)a - \theta_A + \frac{4}{\pi a^3} = 0$$



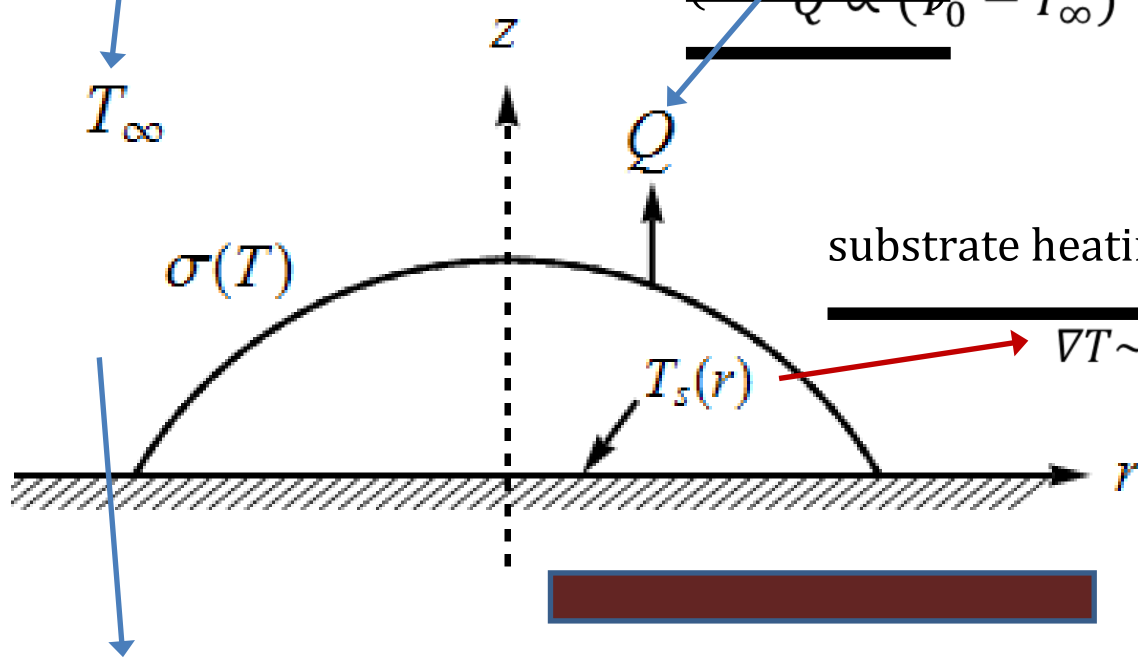


Heating conditions

ambient temperature

heat transfer

[redacted] $- T_\infty)$ → $\nabla T \sim \frac{\Delta T_v}{\Delta z}$



substrate heating (non-uniform)

[redacted] $\nabla T \sim$ / Δr

equation of state

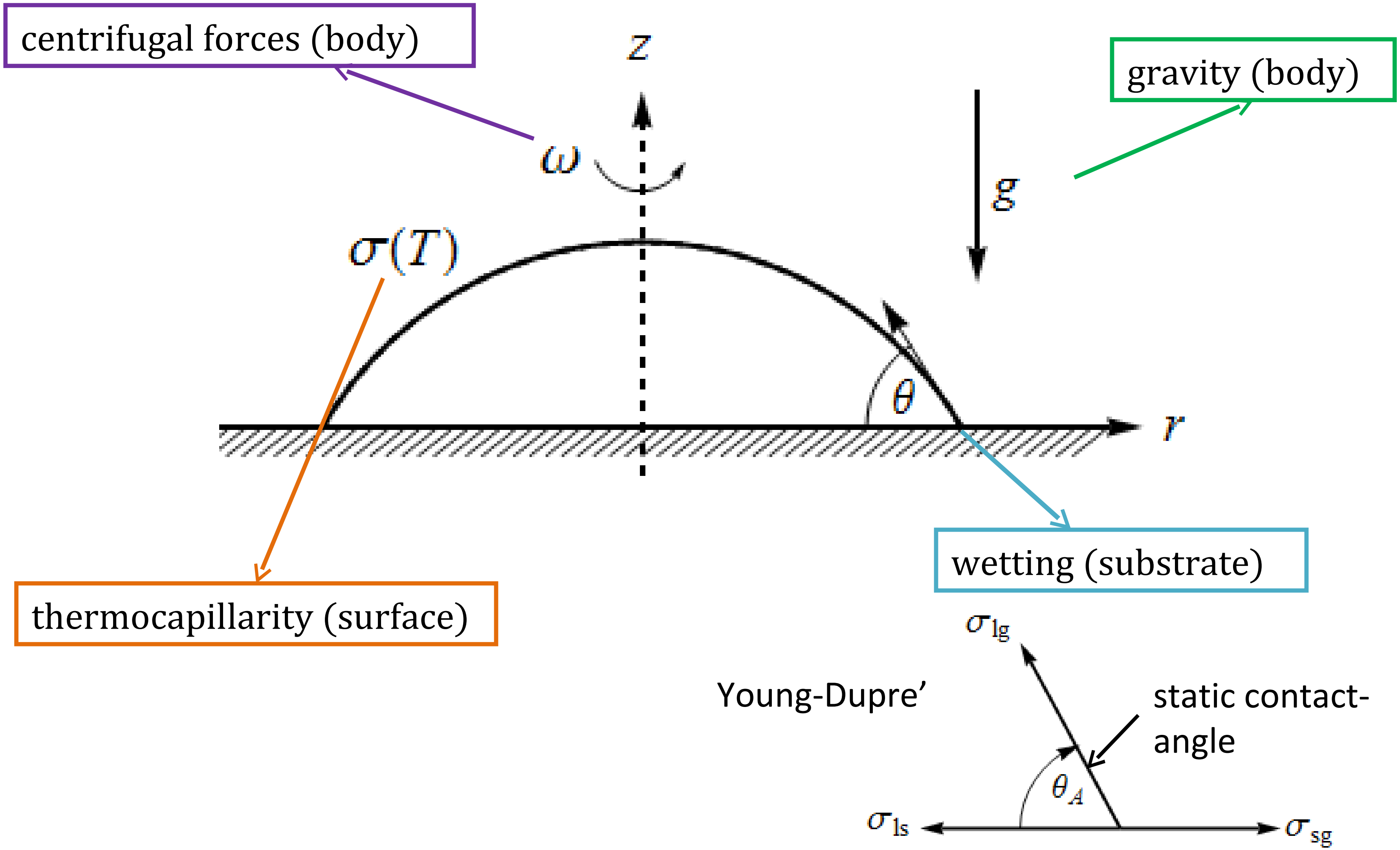
[redacted] $- T_0)$

Marangoni stress (shear)

[redacted]

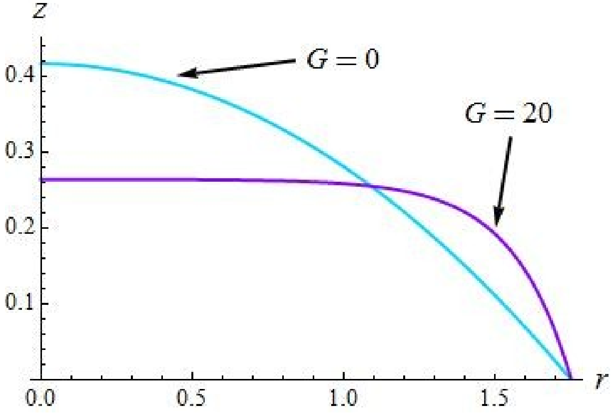
Experiments by Behringer group (Duke University)

Why do fluids spread?

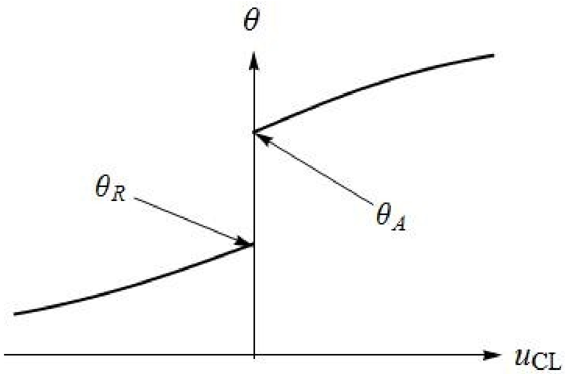


Gravity-driven spreading

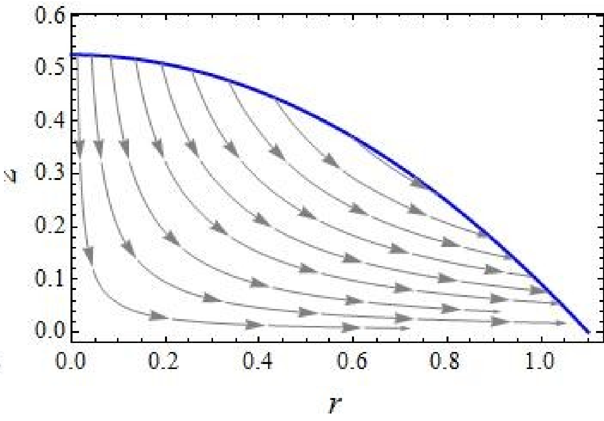
equilibrium shapes



spreading law



base flow



force balance

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{G}{2\pi a}\frac{\mathcal{I}(\sqrt{G}a)}{\left(\sqrt{G}a - 2\mathcal{I}(\sqrt{G}a)\right)}$$

surface tension dominant

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{4}{\pi a^3}$$

gravity dominant

$$\left(\frac{da}{dt}\right)^{1/m} + \theta_A = \frac{\sqrt{G}}{2\pi}\frac{1}{a^2}$$

power laws

$$a(t) \sim t^{\frac{1}{3m+1}}$$

$$a(t) \sim t^{\frac{1}{2m+1}}$$

Quasi-static limit (*C* → *0*)

equilibrium

$$\left(h_{rr}+\frac{1}{r}h_r-Gh\right)_r+\Omega^2 r+\frac{3}{2}\frac{1}{h}\left(\hat{N}+\hat{M}h_r\right)=0$$

time-dependence in BC

$$h_r=h_{rrr}=0\Big|_{r=0}$$

$$h(a(t),t)=0$$

$$\frac{\partial h}{\partial r}(a(t),t)=-\theta(t)$$

$$2\pi\int_0^{a(t)} rh(r,t)\mathrm{d}r=1$$

$$\frac{da}{dt}=(\theta(t)-\theta_A)^m$$

Marangoni numbers

$$\hat{N}=\frac{NC}{\Delta C},\quad \hat{M}=\frac{BC}{\Delta C}$$

Map the problem to the contact line!

Results

- Large parameter space $a_{\infty}\left(\Omega^2, G, \hat{M}, \hat{N}, \theta_A\right)$
- Unforced spreading (base-flow)
  - power laws
- Spreading by thermal-gradients (forced)
  - axial vs. radial gradients
    - similarities, mechanisms and power laws
  - equilibrium, stability and bifurcation
    - surface chemistry (wetting)
  - bi-stability
    - competition