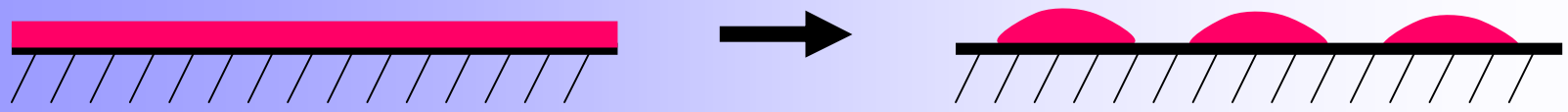
dewetting

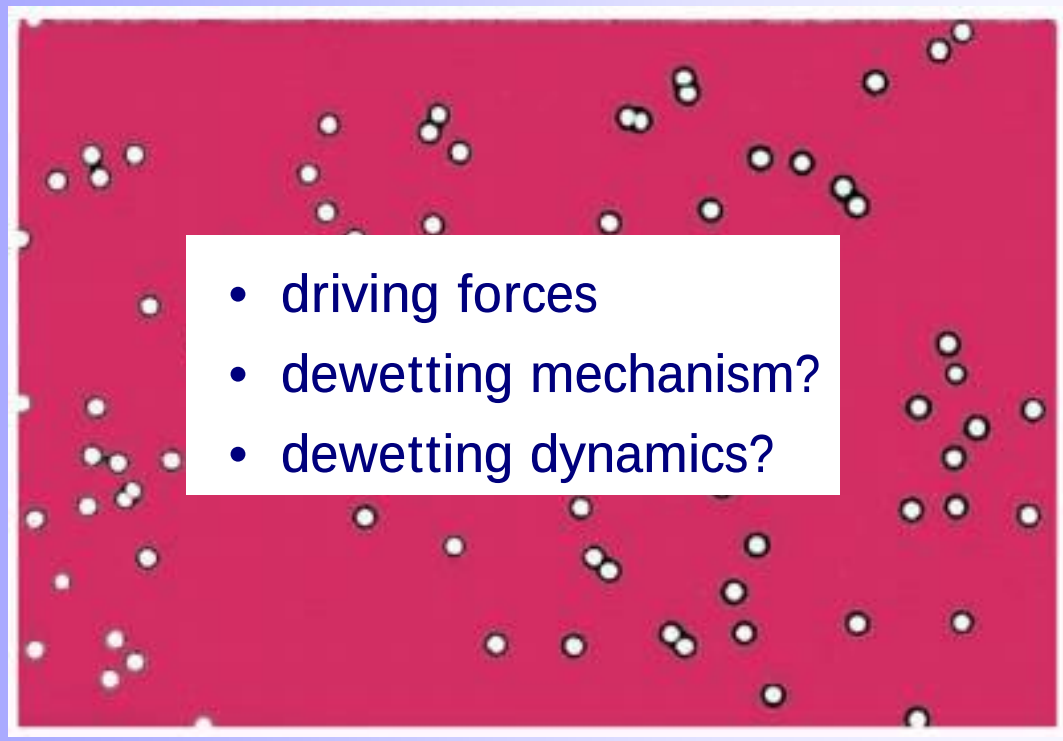


initial state:

continuous film of partially wetting liquid

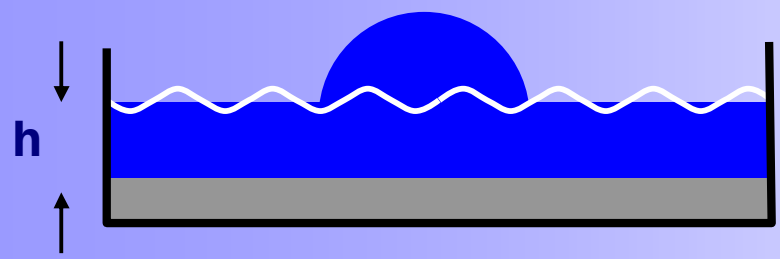
final equilibrium state:

drops with $q = q_Y$



- driving forces
- dewetting mechanism?
- dewetting dynamics?

free energy vs. film thickness



water drop on teflon: q_Y=120°

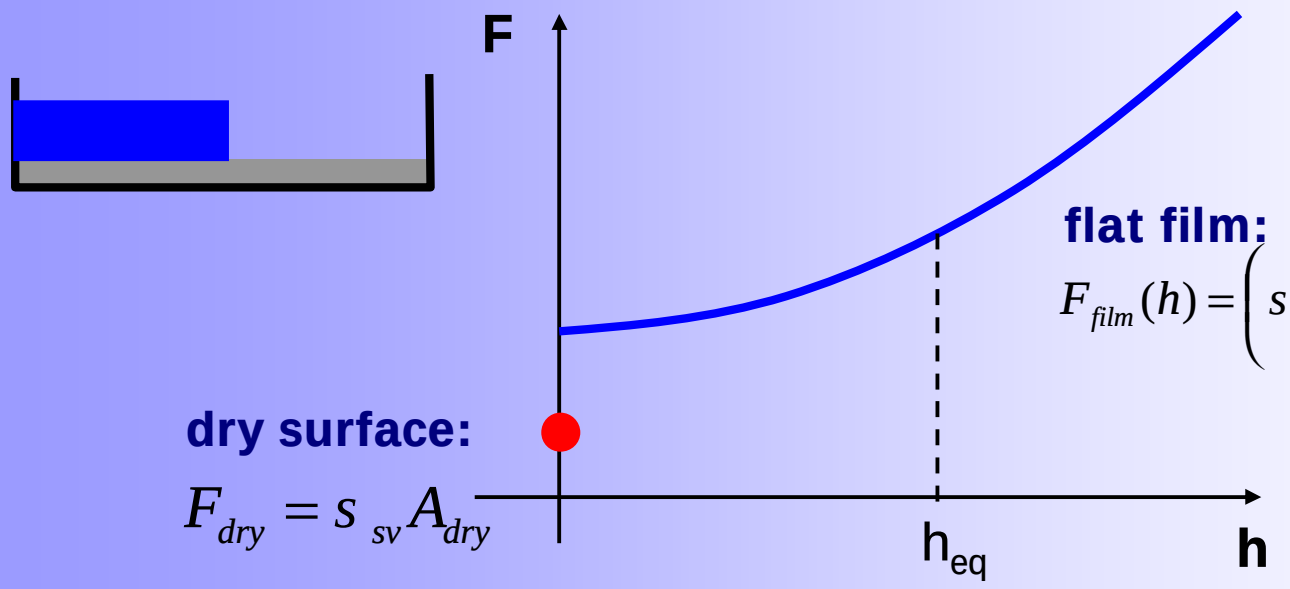
water film with thickness *h*

- **small volume:**
  equilibrium configuration = drop with c.a. q_Y if h is not too large
- **large volume: equilibrium configuration = thick film**
- **stability analysis: film is always stable against perturbations**

à what is the critical volume (thickness) below which the film is unstable?

à how do unstable films break up?

global stability



flat film:

$$F_{film}(h) = \left(s_{sl} + s_{lv} + \frac{1}{2} r\, g\, h^2 \right) A_{film}$$

dry surface:

$$F_{dry} = s_{sv} A_{dry}$$

energy of film + dry patch: $F(A_{dry}) = \left(s_{sl} + s_{lv} + \frac{1}{2} r\, g\, h^2 \right) A_{film} + s_{sv} A_{dry} \overset{!}{=} \min$

$$A_{film} + A_{dry} = A = const. \qquad V = A h_0 = A_{film} h = const.$$

partial wetting:

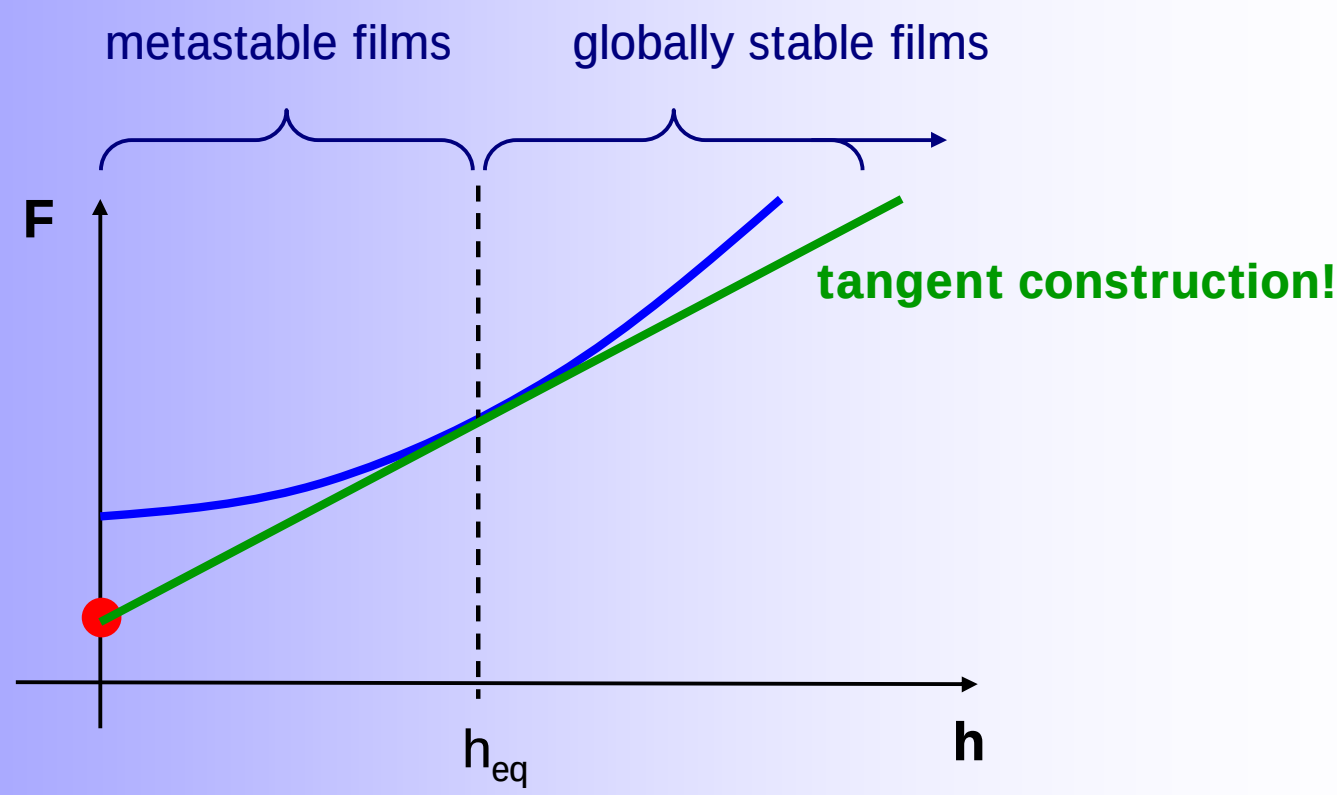
$$S = s_{sv} - (s_{sl} + s_{lv}) < 0$$
$$= s_{lv}(\cos q_Y - 1)$$

$$h_{eq.} = l_c \sqrt{2(1 - \cos q_Y)} = 2 l_c \sin^2 q_Y / 2$$

height of a liquid pancake

Physics of Complex Fluids

global stability (II)



$h_0 > h_{eq}$: film is globally stable

$h_0 < h_{eq}$: film is globally unstable against breakup

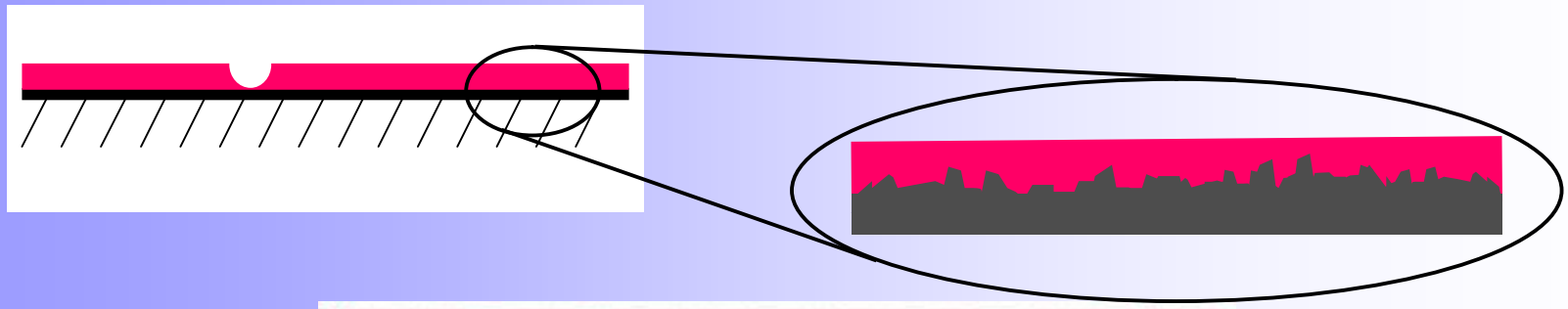
... but locally stable against small perturbations

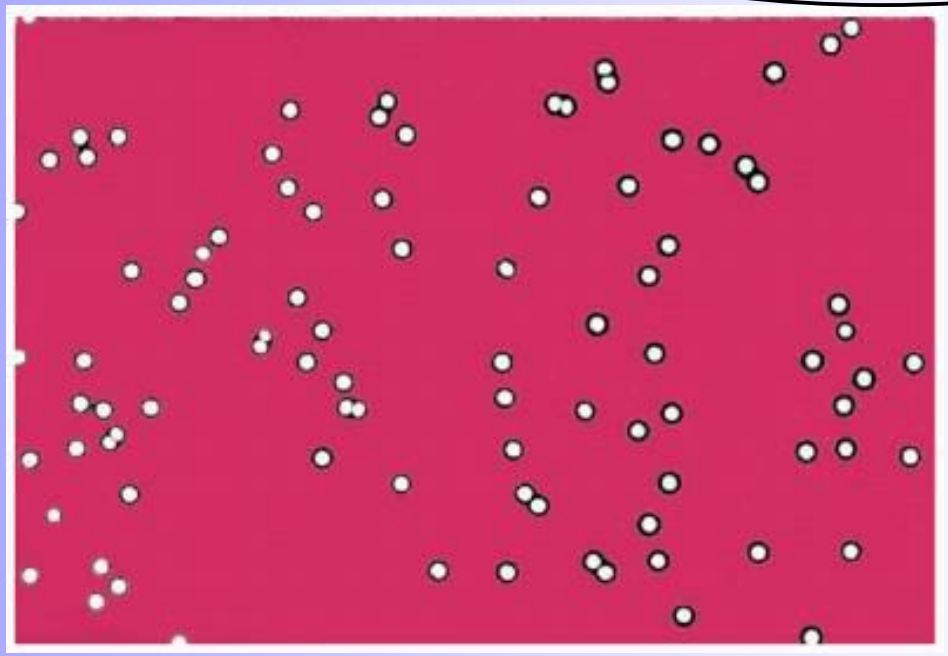
à metastable

a practical experiment …

nucleation barrier >> $k_B T$: create defect to initiate dewetting

nucleated dewetting



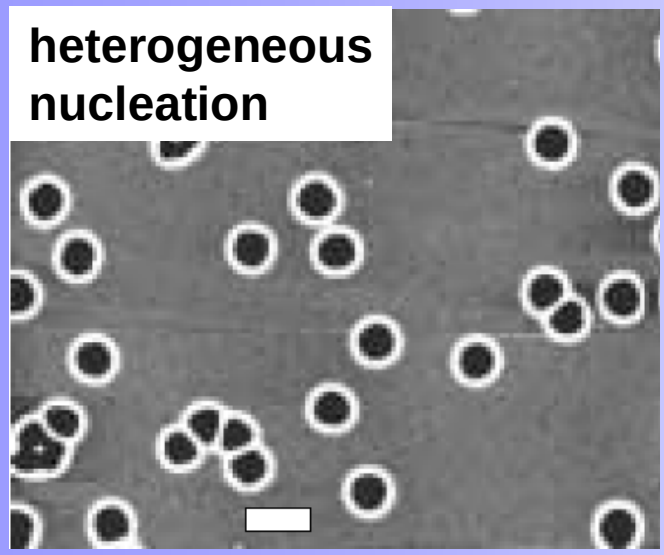


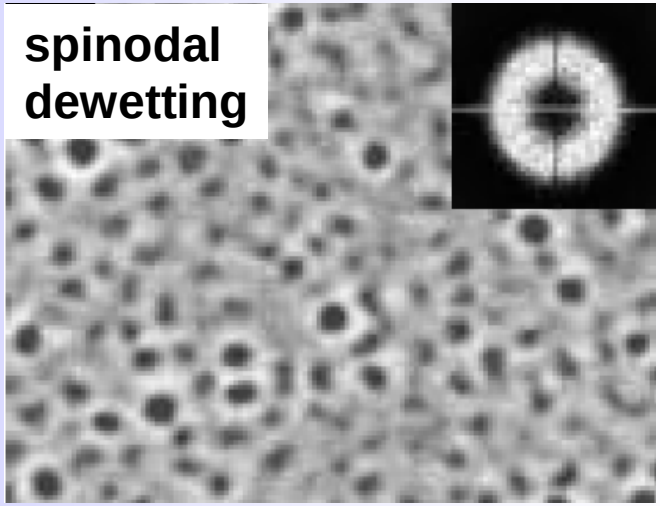
hole nucleation at defect sites (e.g. due to surface roughness, chem. heterogeneity, ...)

à random distribution of hole locations and time of appearance

a second dewetting scenario

polystyrene films on Si





holes appear at random locations and at random times

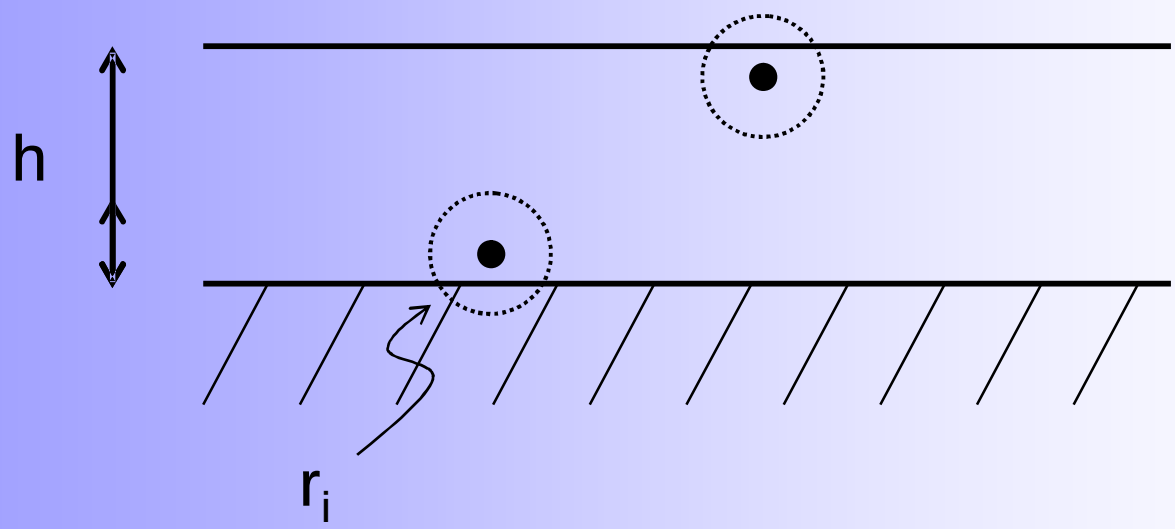
holes appear at regular distances and at the same time

à hallmarks of a linear instability

 Seemann et al. Phys. Rev. Lett. 2001

wetting and long-range forces

disjoining pressure and effective interface potential (II)



$h >> r_i$: $F = s_{sl} + s_{lv}$

$h = O(r_i)$: $F = F(h) = s_{sl} + s_{lv} + \Phi(h)$

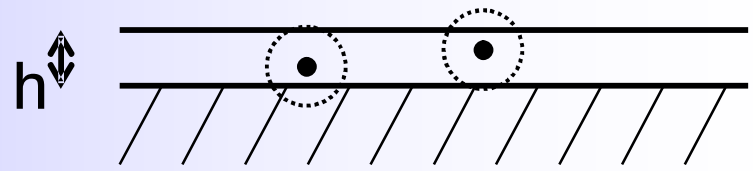
$\Phi(h)$: effective interface potential

properties of F(h)

$$\Phi(h) = F(h) - (s_{sl} + s_{lv})$$

$$h \to \infty: \quad \Phi \to 0$$

$$h = 0: \quad \Phi = s_{sv} - (s_{lv} + s_{sl}) = S$$



O(F) = O(s) [10 ... 100 mJ/m^2 (typical organic liquids)]

$\Phi(h)$: interaction energy / unit area of adjacent interfaces

$$-\frac{d\Phi}{dh} = \Pi(h)$$ force / unit area between interfaces: „disjoining pressure“

example: van der Waals interaction

$$\Phi(h) = \frac{A}{12p\ h^2}$$

A: Hamaker constant

A=f(n_v,n_l,n_s,ε_v,ε_l,ε_s)

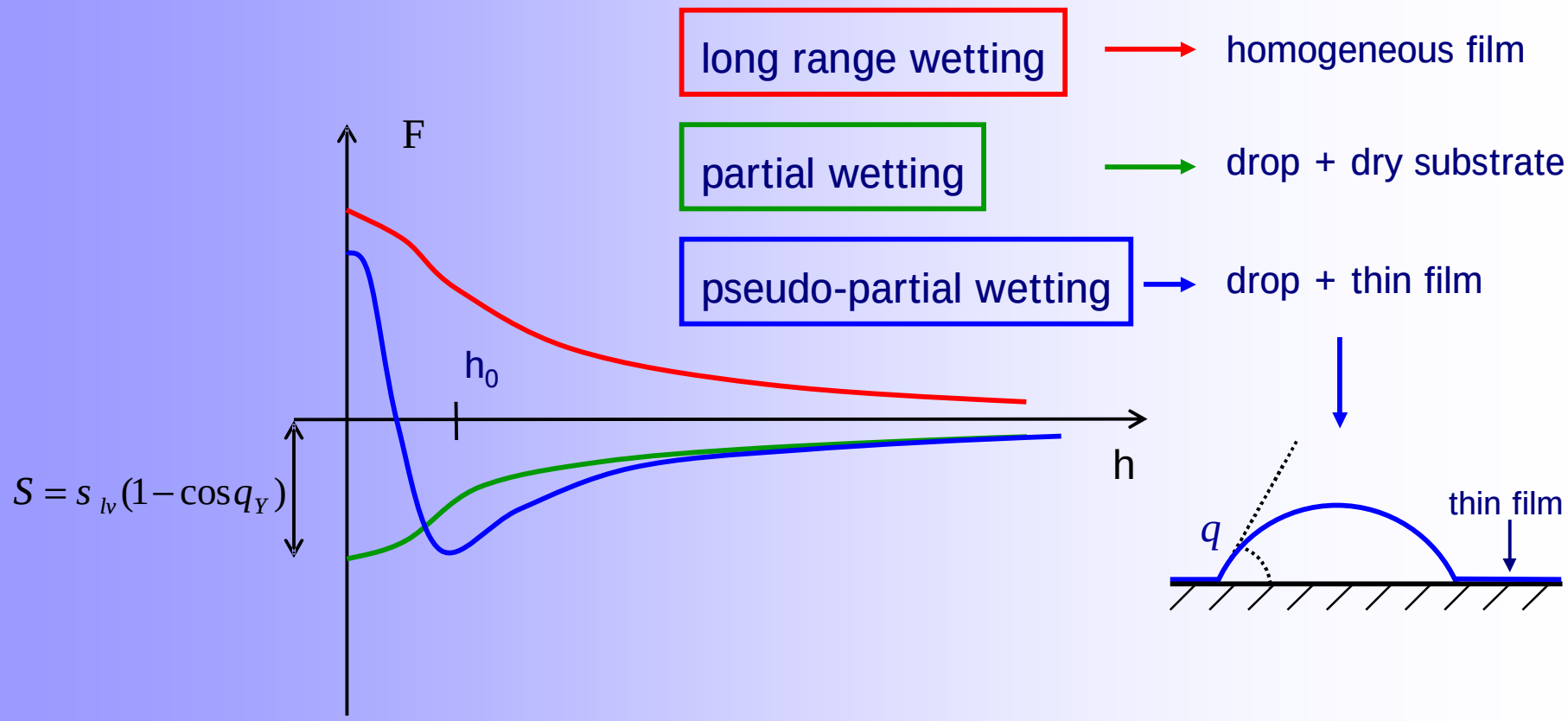
O(A)=10^{-20} J (≈2.4k_BT @ RT)

Physics of Complex Fluids

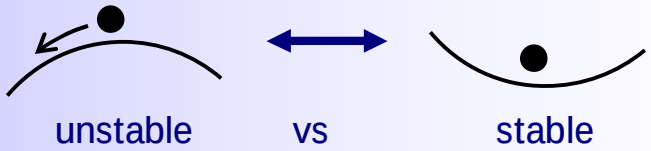
contributions to disjoining pressure

- van der Waals interaction $\Phi(h) = A/12p\ h^2$
- electrostatic interaction (“double layer forces”)
- structural solvation forces
- hydrogen bonding forces
- short-range chemical forces

F and macroscopic wetting

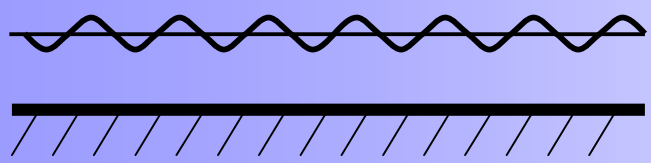


comment on stability:



Physics of Complex Fluids

stability of thin wetting films



thin film equation:

$$\partial_t h = \frac{1}{3m}\frac{d}{dx}\left(h^3 \partial_x P\right) = \frac{h_0^3}{3m}\partial_{xx} P$$

small perturbation:

$$h(x,t) = h_0 + dh(t)\cdot\cos qx \qquad dh << h_0$$

local pressure: $P(x,t) = -s\ \partial_{xx} h + \left.\frac{d\Phi}{dh}\right|_{h(x)}$

$$\left.\frac{d\Phi}{dh}\right|_{h(x)} \approx \Phi'(h_0) + \Phi''(h_0)\cdot dh$$

$$\boxed{d\dot{h}(t) = -\frac{h_0^3}{3m} q^2 \left(s\ q^2 + \Phi''(h_0)\right) dh(t)}$$

F" > 0: film locally stable for all *q*

F" < 0: film locally stable for large *q* but unstable for small *q*

stability of thin wetting films (II)

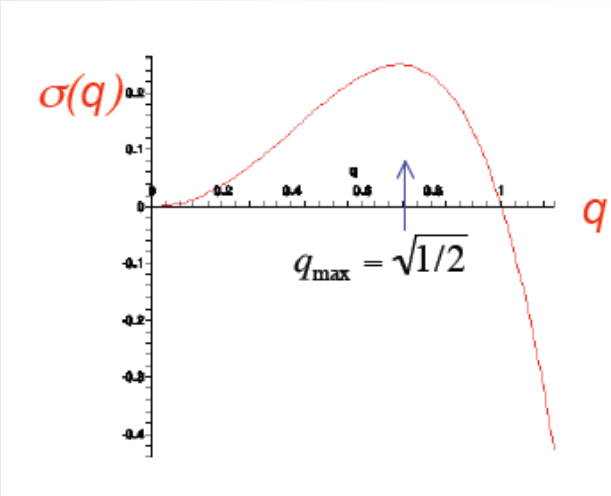
critical wavevector: $q_c = \sqrt{|\Phi''(h_0)| / s}$

fastest growing mode:

maximum of prefactor $q^* = q_c / \sqrt{2}$

characteristic growth time: $t^* = \dfrac{12m}{h_0^3 q_c^4 s}$

van der Waals: $t^* \propto h_0^5$

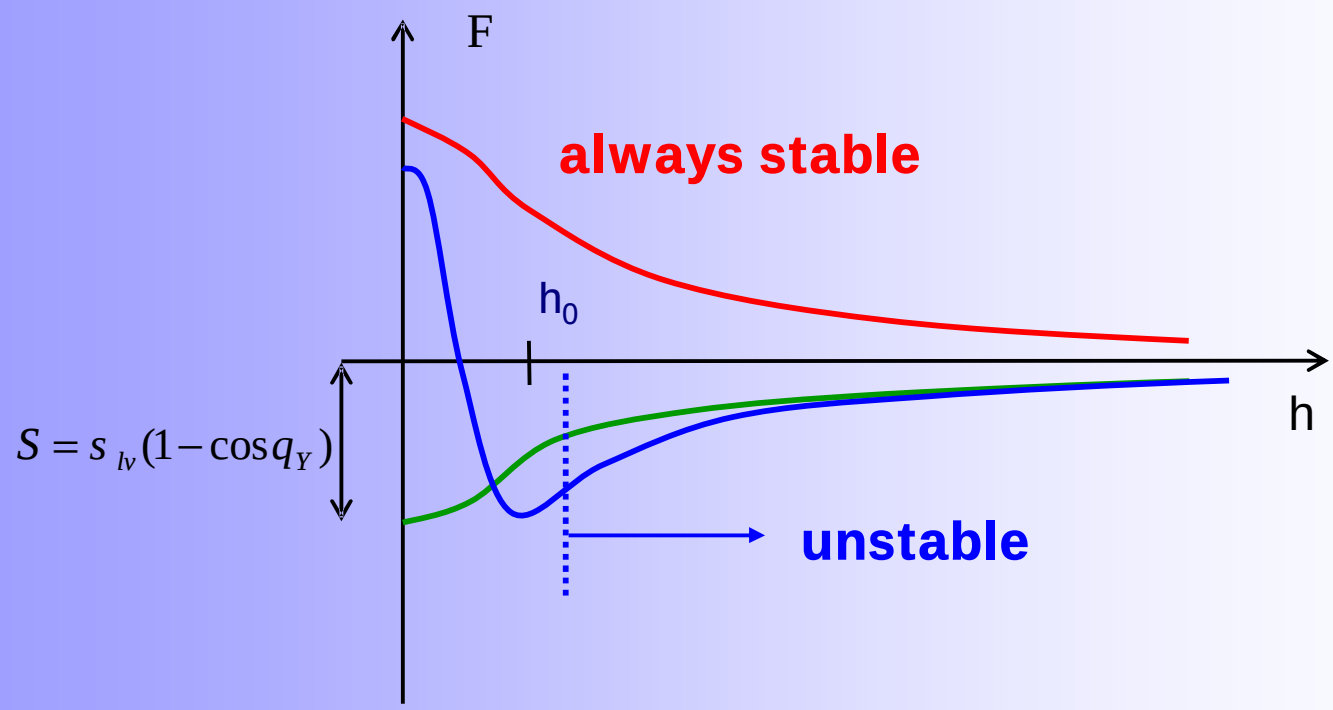


à thin films with an initial thickness,

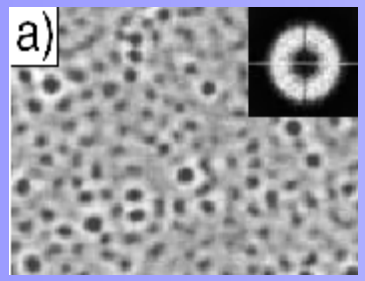
for which F”<0 are linearly unstable

Physics of Complex Fluids

interface potential & stability



example of a complex interfacial potential



$$\Phi(h) = \frac{c_8}{h^8} - \frac{A_{air-PS-SiO2}}{12p}\left(\frac{1}{h^2} - \frac{1}{(h+d)^2}\right) - \frac{A_{air-PS-Si}}{12p\,(h+d)^2}$$

short range chemical force

vdW: air-liq.-SiO

vdW: air-liq.-Si

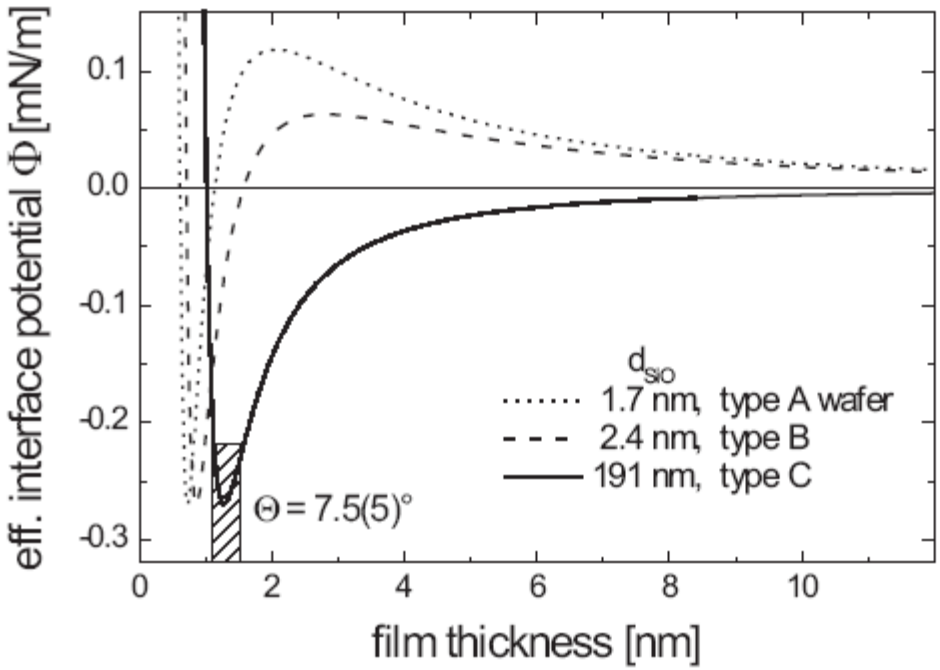
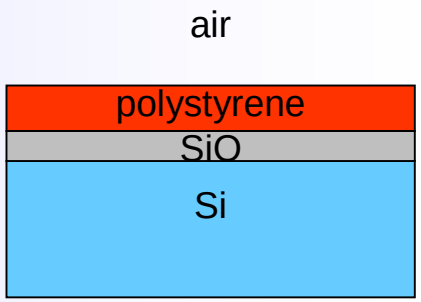


Figure 4. Reconstructed effective interface potentials $\Phi(h)$ for PS films on three types of substrate, taken from reference [23]. The hatched rectangle indicates in the x-direction the experimental error in determining $h^\star$ and in the y-direction the error in $\Phi(h^\star)$ due to the limited accuracy of the contact angle measurement.

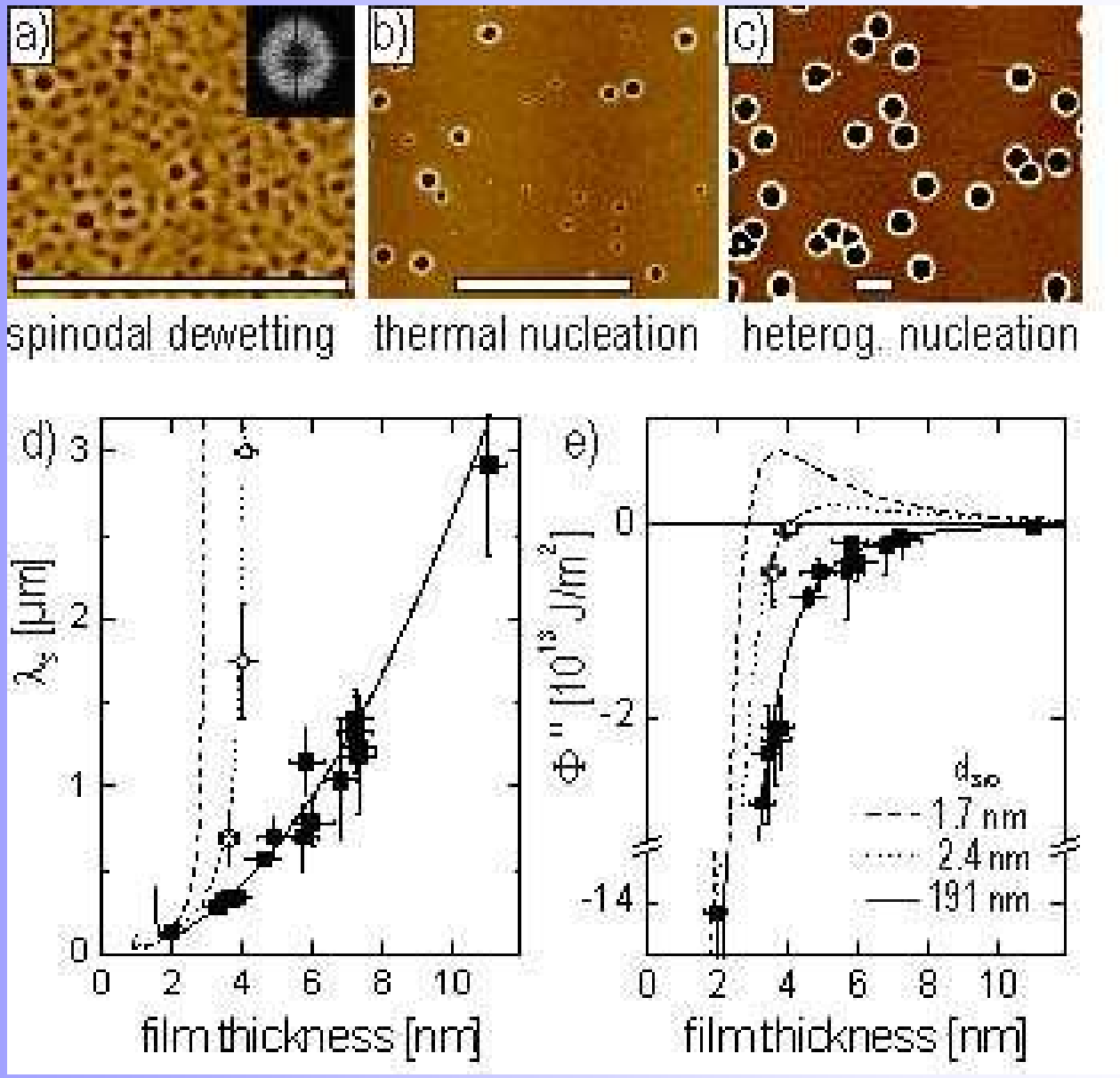


layered substrates: SiO:Si

Seemann et al.
J. Phys. Cond. Matt. 13, 4925 (2001)

Physics of Complex Fluids

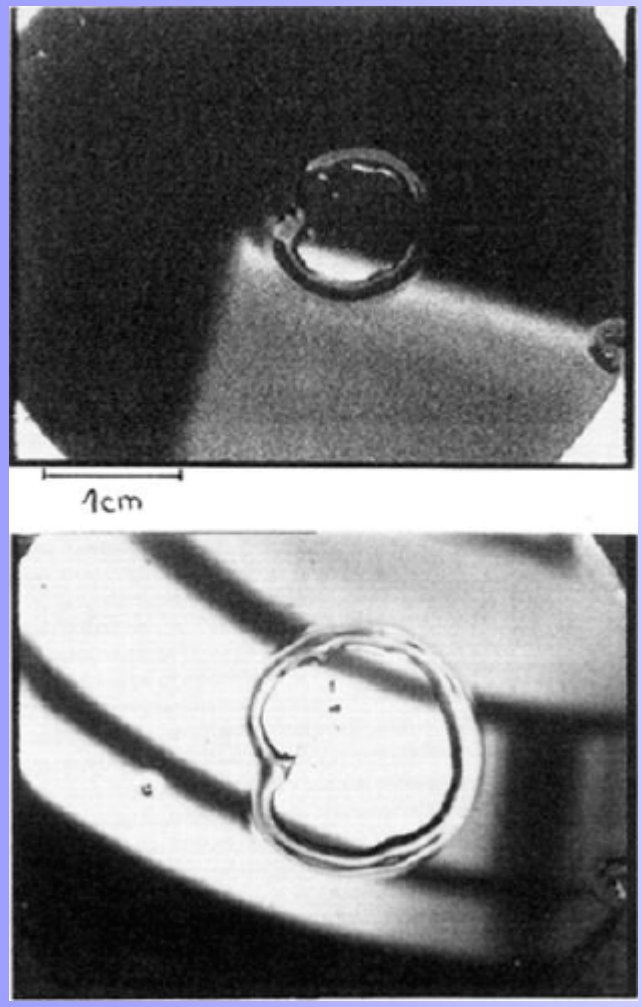
various dewetting scenarios

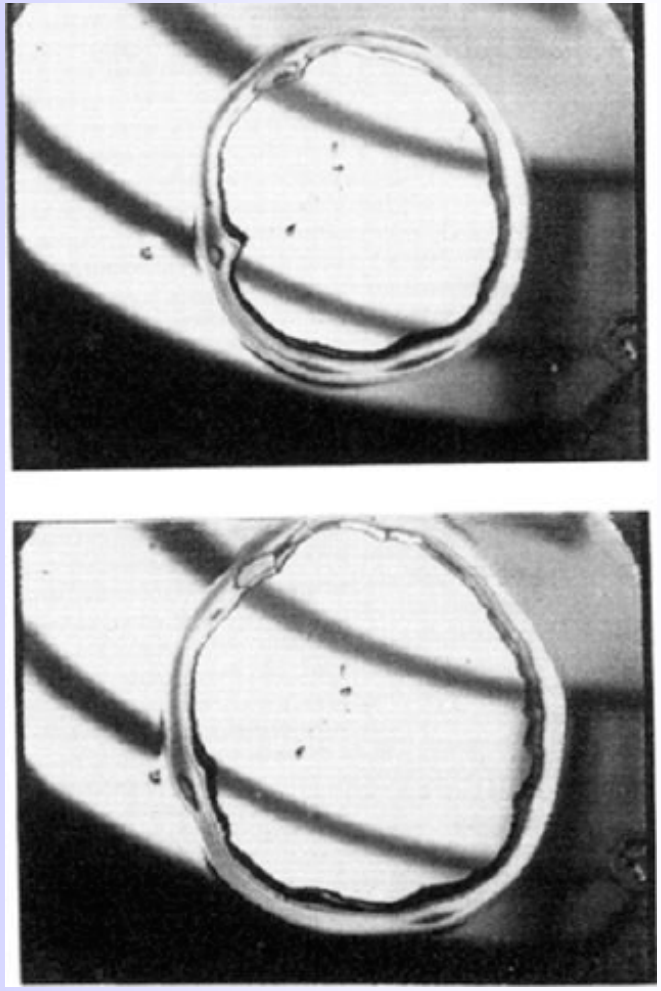


Seemann,
Jacobs,
Herminghaus

Physics of Complex Fluids

dewetting dynamics

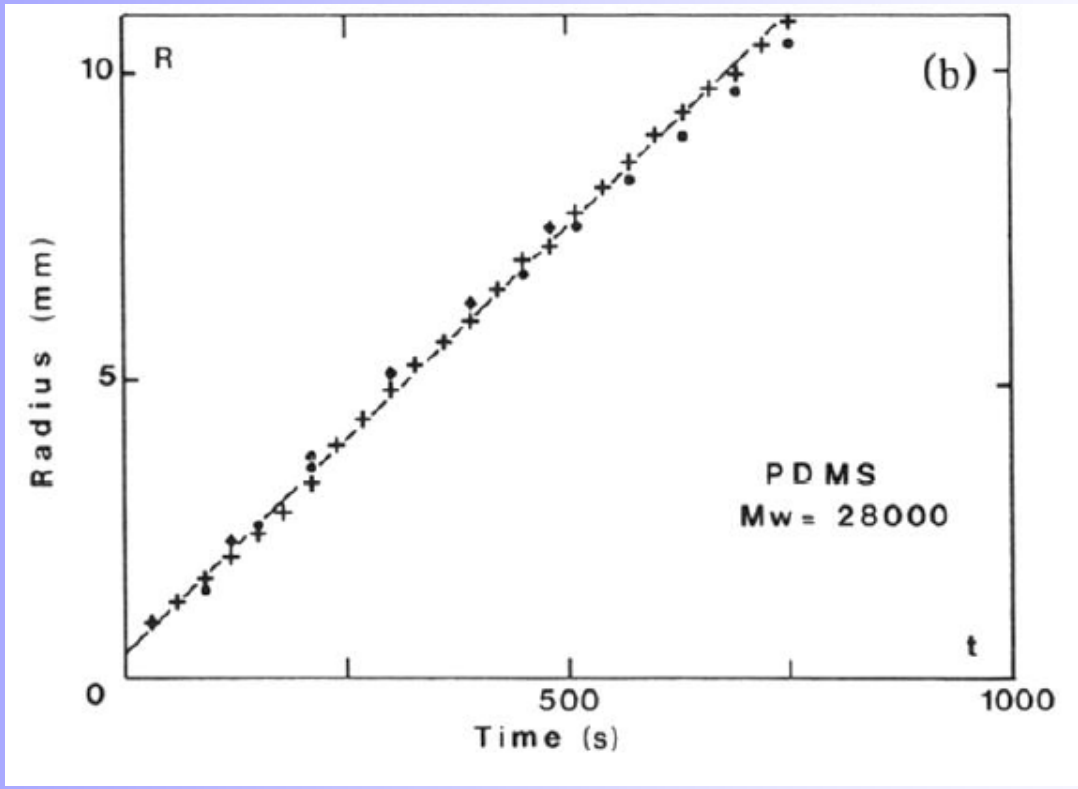




PDMS (30 µm) on fluorinated Si

 Redon et al. Phys. Rev. Lett. 1991

dewetting dynamics



observations:

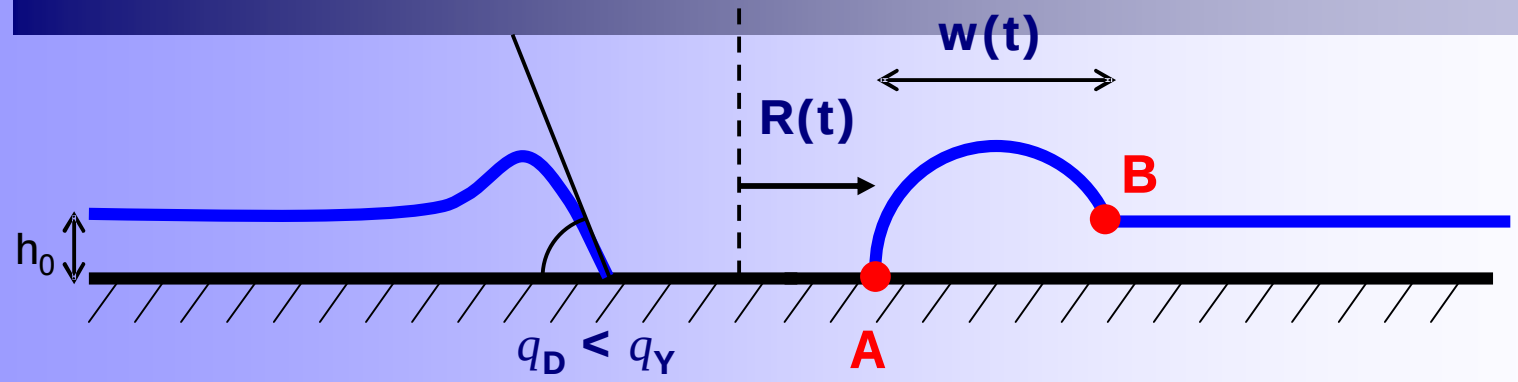
- excess material collects in rim

- constant dewetting velocity v

- dewetting velocity v ~ q_Y^3

Redon et al. Phys. Rev. Lett. 1991

model



assumptions:

- $h_0 << w << R$; $q << 1$
- rim profile is circular and symmetric
- rim volume: $V_{rim} = pR^2 h_0$

dynamics: balance of viscous dissipation & imbalanced Young force

$$\frac{3mV^2}{q_D}\ln\frac{w}{a} = D = \iint m\,(\partial_z v)^2\,dx\,dz = s\,(\cos q_Y - \cos q_D)\cdot V = V\frac{s}{2}(q_Y^2 - q_D^2)$$

point A & B: $V_A = \frac{s}{6m\,l_A} q_D (q_Y^2 - q_D^2)$ $\qquad V_B = -\frac{s}{6m\,l_B} q_D (0 - q_D^2) = \frac{s}{6m\,l_B} q_D^3$

$V_A = V_B$: $\quad q_D = \frac{q_Y}{\sqrt{1 + l_A / l_B}} = const.$ **à** V=const. ~q_Y^3

Physics of Complex Fluids