FLOW

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Wetting contact angle

Minh Do-Quang

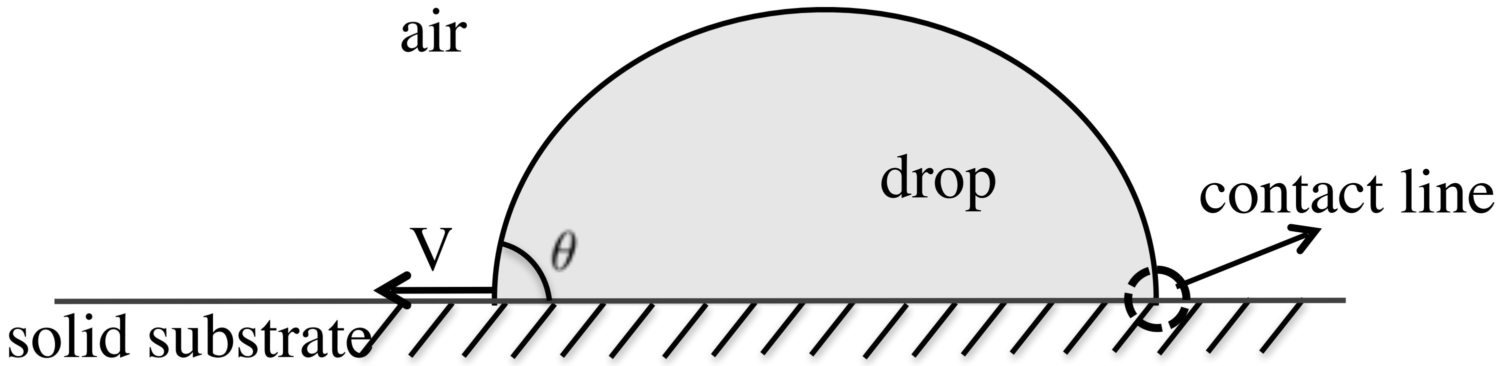
KTH VETENSKAP OCH KONST

Outline

- Statics; capillarity and wetting
- Dynamics; models describing dynamic wetting
  - Hydrodynamics (Tanner-Cox-Voinov law)
  - Molecular kinetics theory
- Dynamical wetting transitions; from slip to splash
- Phase field model developed to study wetting
- Simulations and experiments of short-time spontaneous capillary driven spreading
  - Physical mechanisms believed to govern dynamic wetting

Contact line

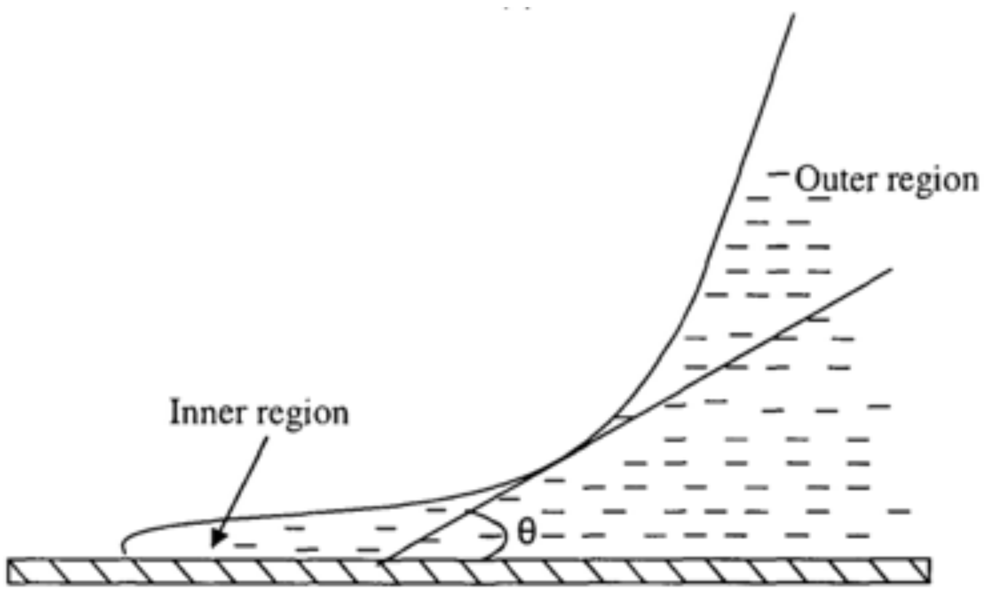
- Contact line is the point where an interface meets a solid substrate.



- Multi-scale problem, typical experimental drop size ~1mm, relevant length scale of the interface ~1nm

Why study contact lines?

- Still unresolved physical problem, with great challenges in both modeling and experiments
  - Multiscale problem (inner/outer) (from molecular to millimetric)
  - Singular problem (inner) (Divergence of viscous stress)
- Important in many industrial processes: Coating, microfluidic systems, sintering, lithography techniques ect.



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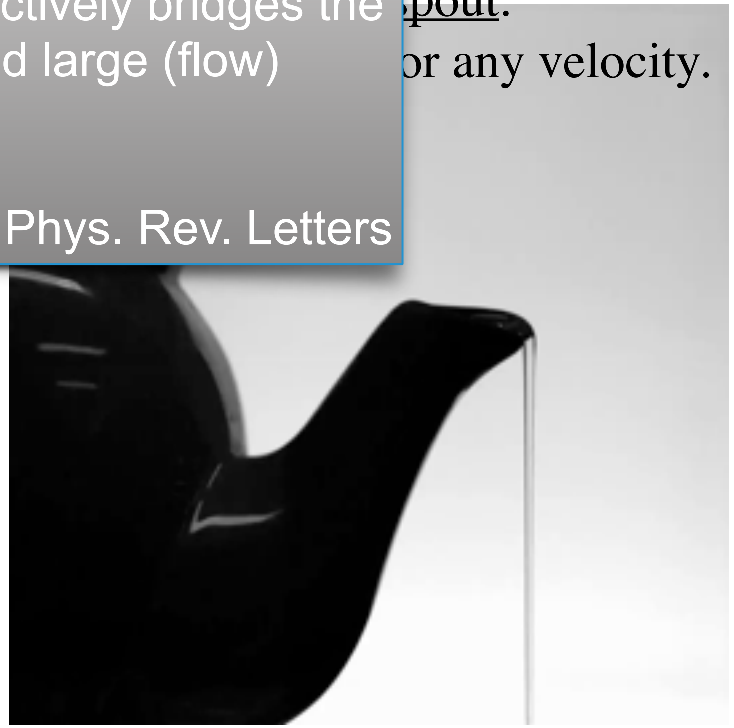
<u>Hydrophilic</u> <u>spout</u>:
Water flow or any velocity.
spout as the

This is an inertial-capillary adhesion phenomenon, coupling inertial flows to a capillary adhesion mechanism. This phenomenon effectively bridges the gap between the small (surface) and large (flow) scales.

Duez et al., 2010 Phys. Rev. Letters



Fundamental problems of wetting

- Statics problems
  - Hydrodynamics: forces, velocity, stress and singular flow in the vicinity of the interface.
  - Thermodynamics: Gibbs free energy and equilibrium contact angle
  - Physicochemical interaction: surfactant and surface tension
  - Evaporation, electrowetting etc.
- Dynamic wetting
  - Dynamic wetting contact angle theories: dissipation energy
  - Microscopic model: molecular kinetic theory
  - Numerical model: free energy based

Master references

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- P.G. de Gennes et. al – Capillarity and wetting phenomena – Springer (03)
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- Duez, C. et. al - Making a splash with water repellency - Nature Physics, 3 (2007)
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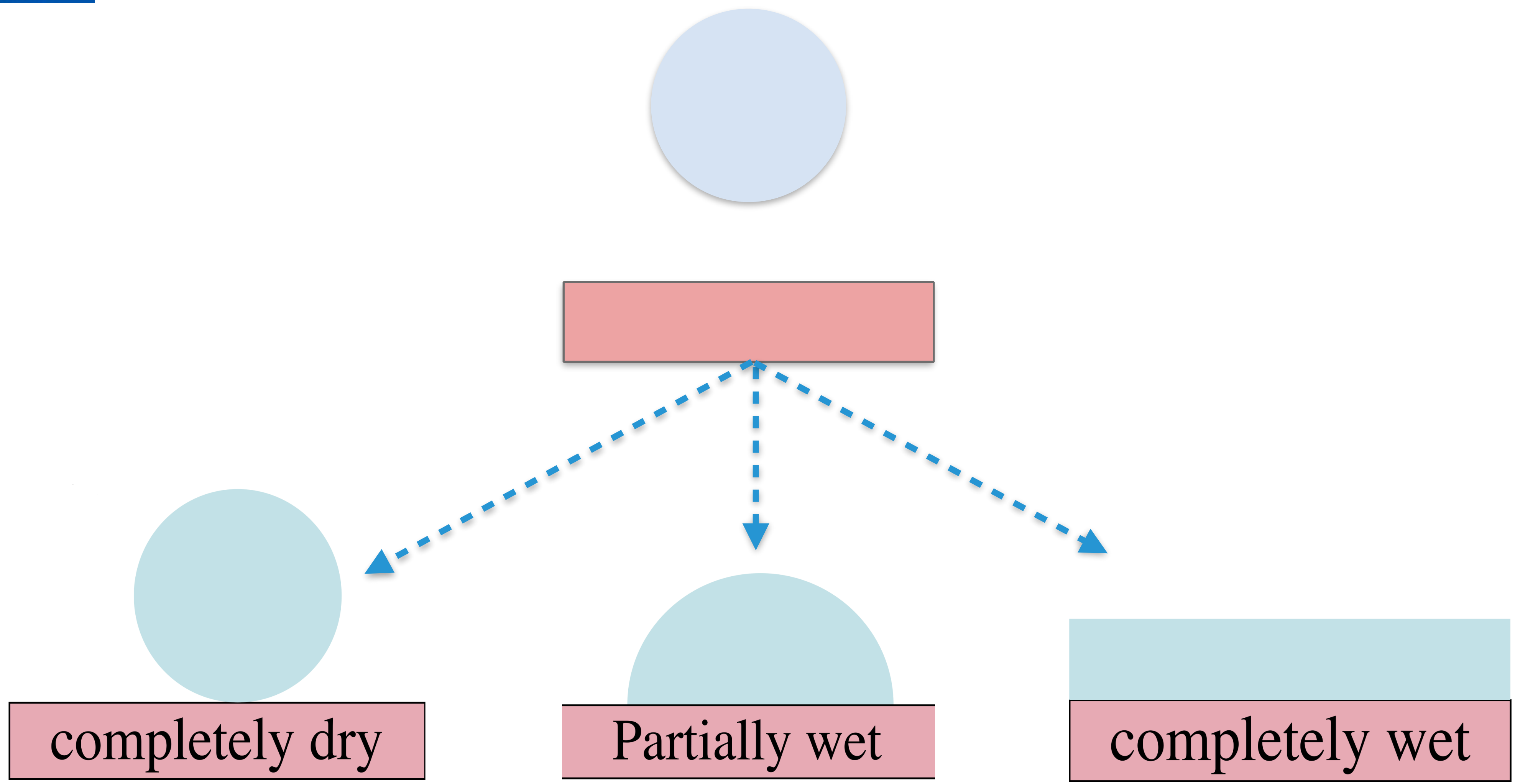
- Bird, J. - Short-Time Dynamics of Partial Wetting. Physical Review Letters, 100 (2008).
- Carlson, A. et. al - Contact line dissipation in short-time dynamic wetting. EPL, 97 (2012).
- Eddi, A., et. al. - Short time dynamics of viscous drop spreading. Physics of Fluids, 25 (2013)

Three different possible wetting states



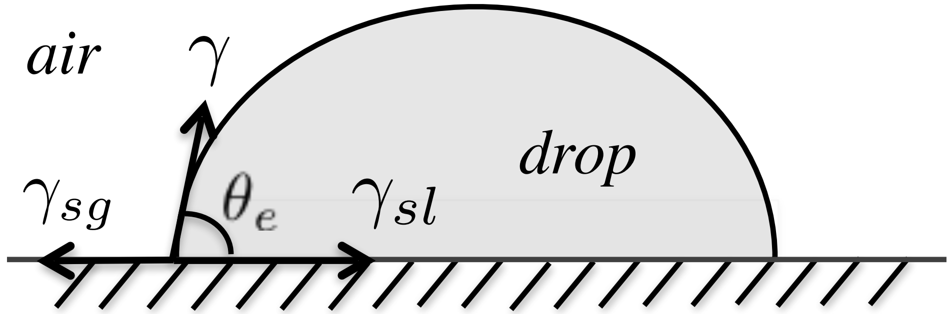
Wetting contact angle, models

Young's equation

Cassie-Baxter model

Wenzel model

Numerics / Experiments



θ_e is the equilibrium contact angle

Substrate surface energy: γ_{sg} (dry)

γ_{sl} (wet)

- Force balance yields Young's law:

$$\cos(\theta_e) = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma}$$

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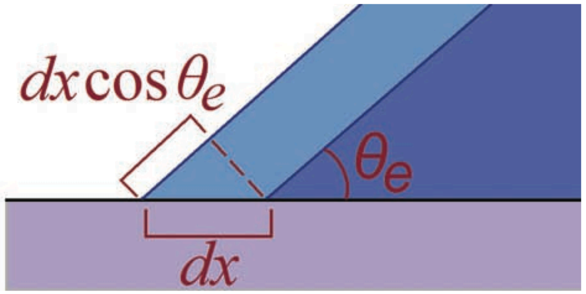
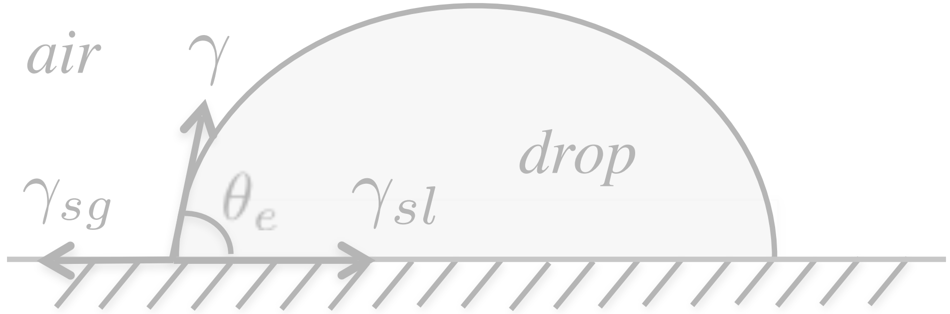


$$dW = \underbrace{(\gamma_{SG}) - \gamma_{SL})dx}_{contact\ line\ motion} - \underbrace{\gamma\cos\theta_e dx}_{creating\ new\ interface}$$

Works done by moving a contact line



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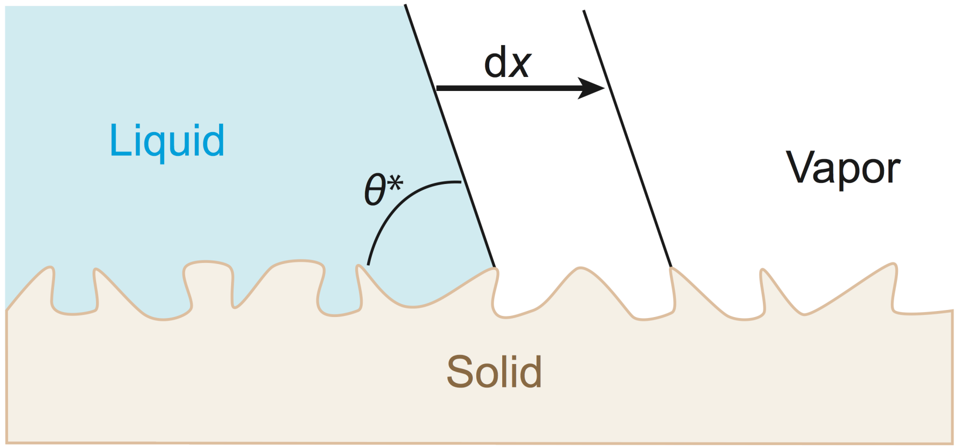

The surface energy variation dW arising from an apparent displacement dx of the line

$$dW = \underbrace{r(\gamma_{SG}) - \gamma_{SL})dx}_{contact\ line\ motion} - \underbrace{\gamma\cos\theta^* dx}_{new\ interface}$$

The Wenzel relation predicts that roughness enhances wettability

$$\cos\theta^* = r\cos\theta$$

$$r = \frac{\text{real surface area}}{\text{apparent surface area}} \geq 1$$

Wetting contact angle, models

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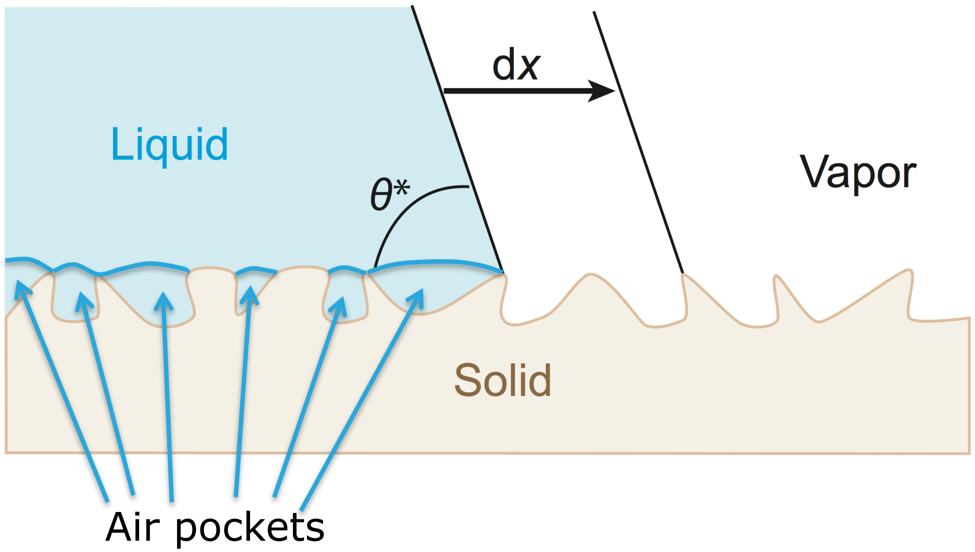
Numerics / Experiments



The surface energy variation dW arising from an apparent displacement dx of the line

$$dW = \underbrace{\phi_S(\gamma_{SL} - \gamma_{SG})dx + (1-\phi_S)\gamma dx}_{contact\ line\ motion} + \underbrace{\gamma \cos\theta^* dx}_{new\ interface}$$

For equilibrium ($dE/dx = 0$),

$$\cos\theta^* = -1 + \phi_S + \phi_S \cos\theta_e$$

$$\phi_S = \frac{\text{Area of islands}}{\text{Projected Area}} < 1$$

Contact Angle Hysteresis

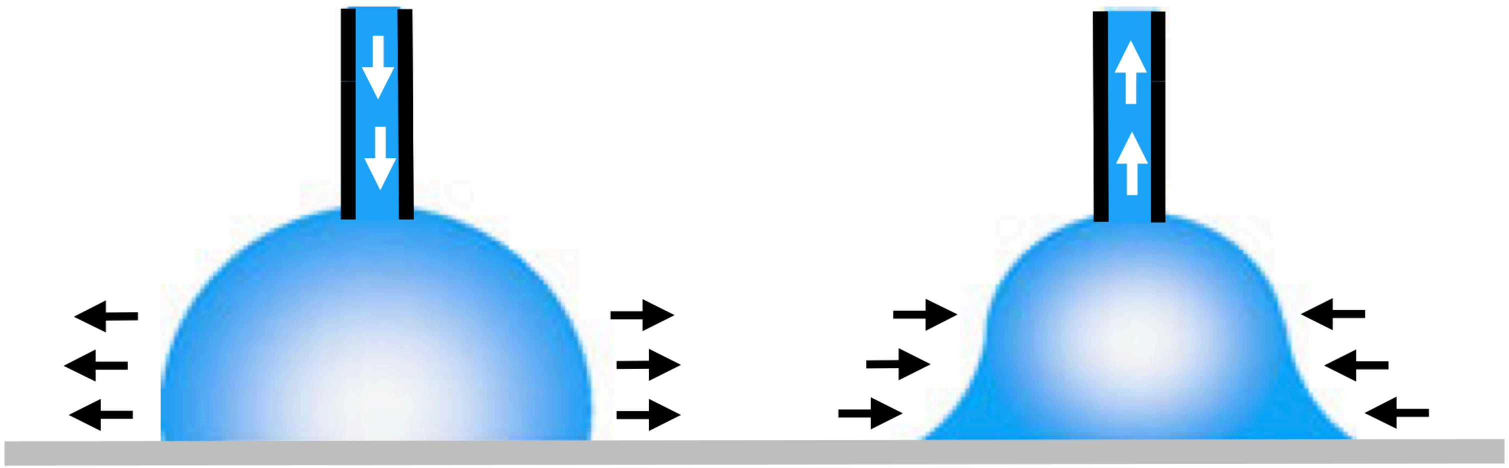
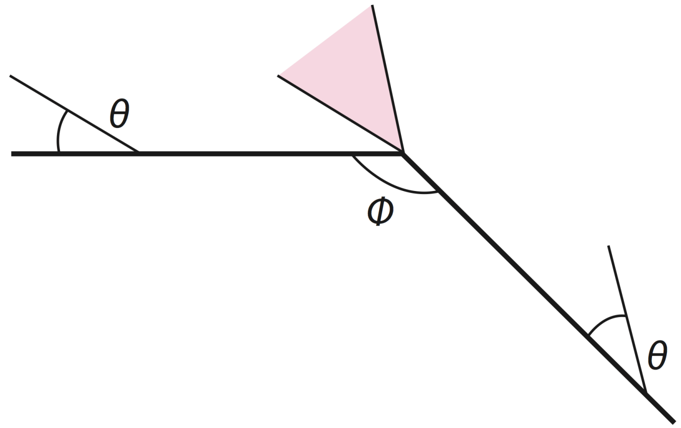


Illustration of advancing and receding contact angles

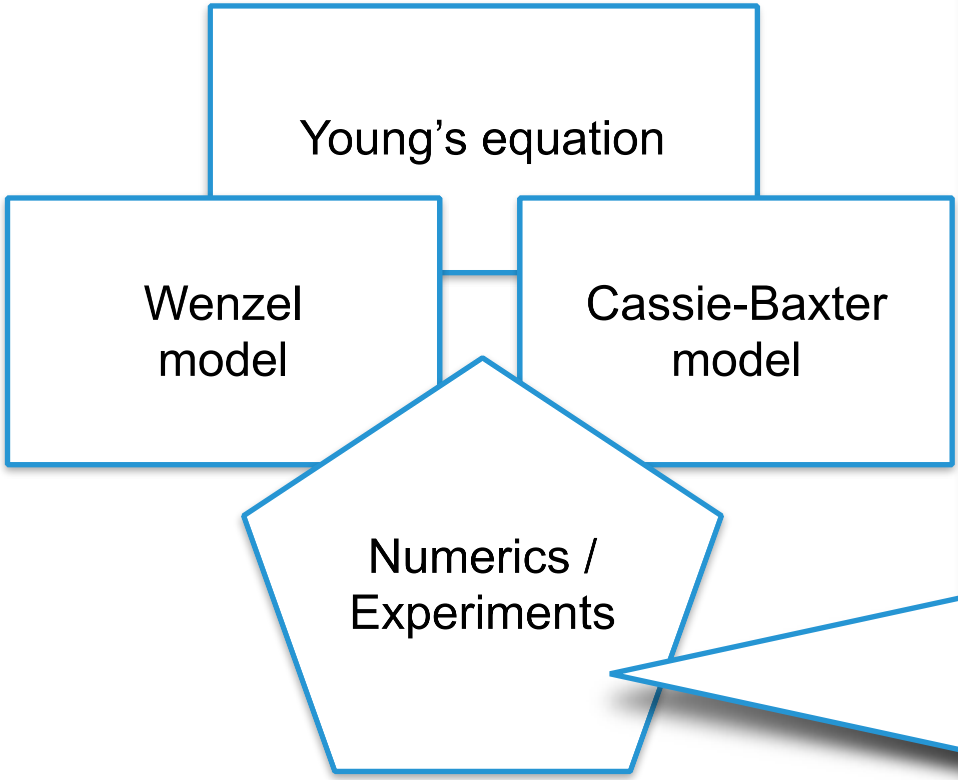
- Dynamic contact angles can be measured at various rates of speed. At a low speed, it should be close or equal to a properly measured static contact angle. The difference between the advancing angle and the receding angle is called the hysteresis (H): $H=\theta a-\theta r$. It arises from surface roughness; and/or heterogeneity or chemical contaminations; or solutes.

Pinning of a contact line on an edge



- The Young condition stipulates that the liquid meets the solid with a contact angle θ. Hence the contact angle at the edge can take any value (if the horizontal direction is considered as the reference one) between θ and $\pi - \varphi + \theta$, as illustrated by the colored region.

Wetting contact angle, models



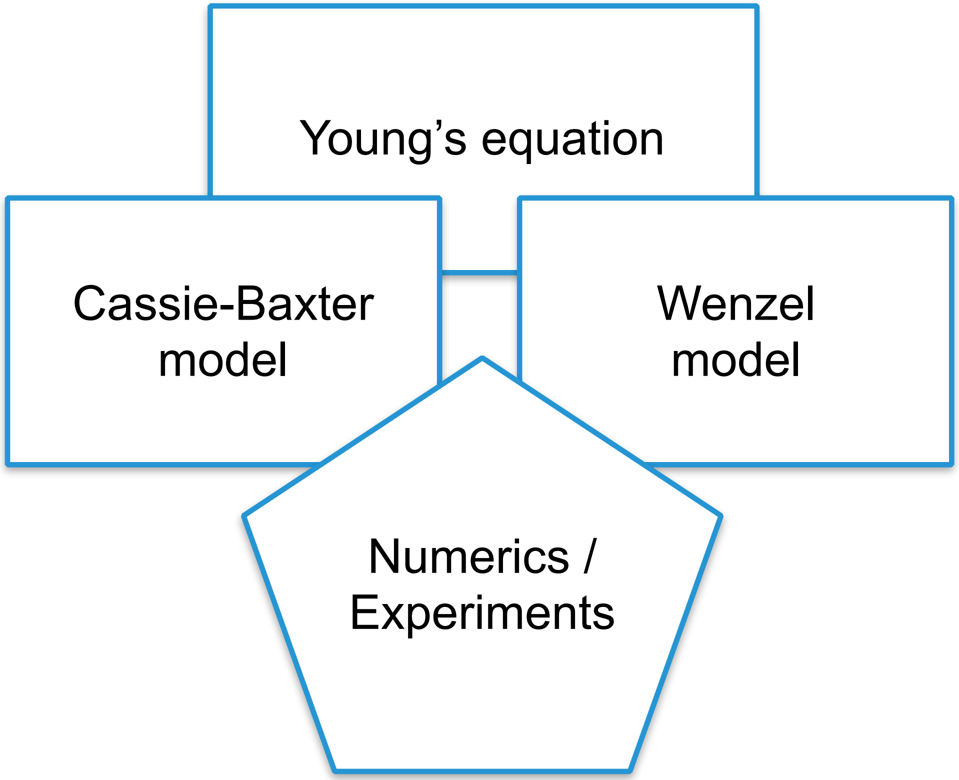
✦Solution of Young-Laplace equation.

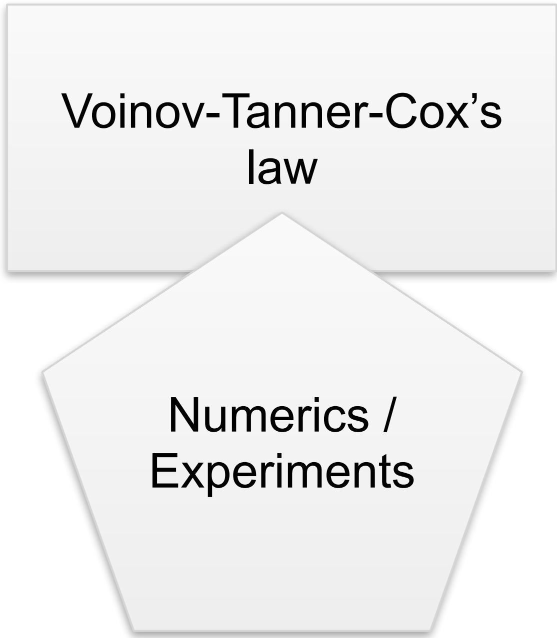
$$P_{in} - P_{out} = \gamma \frac{dA}{dV}$$

✦Darcy’s law for porous media

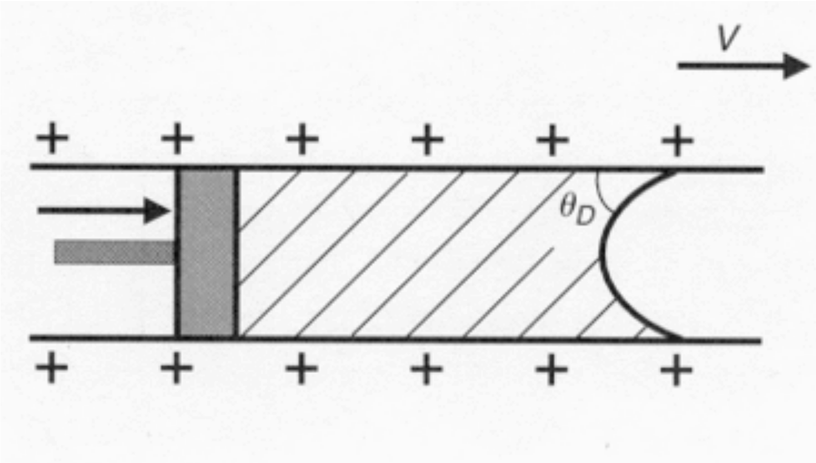
$$\text{Darcy flux } q \equiv vn = -\frac{k}{\mu} \nabla P$$

Summary about the equilibrium and dynamics contact angle



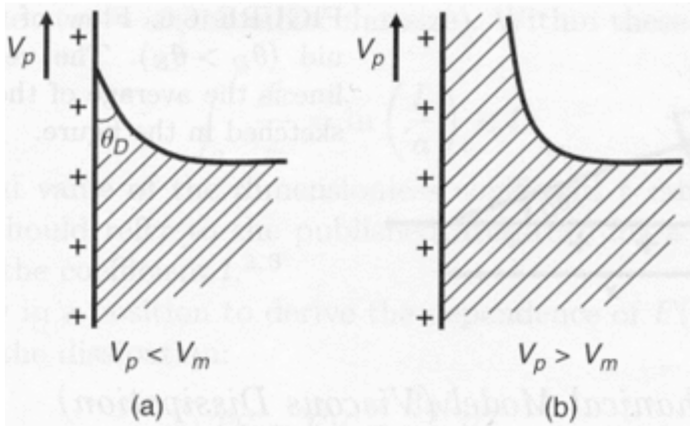


Dynamics of the contact line (Hoffman 1975)



Pushing a liquid in a thin tube, observing the contact angle θ_D

(*Hoffmann exp.*)



Vertical extraction of a plate from a pool of liquid.

- At low pull rates the triple line remains at a fixed height, that is, it moves with V = - Vp relative to the plate.
- At higher pull rates, the triple line moves with a finite thickness. This is called forced wetting

$$F(\theta_D) = \gamma_{SG} - \gamma_{SL} - \gamma \cos\theta_D$$

$F > 0$ $\qquad\qquad$ $F < 0$

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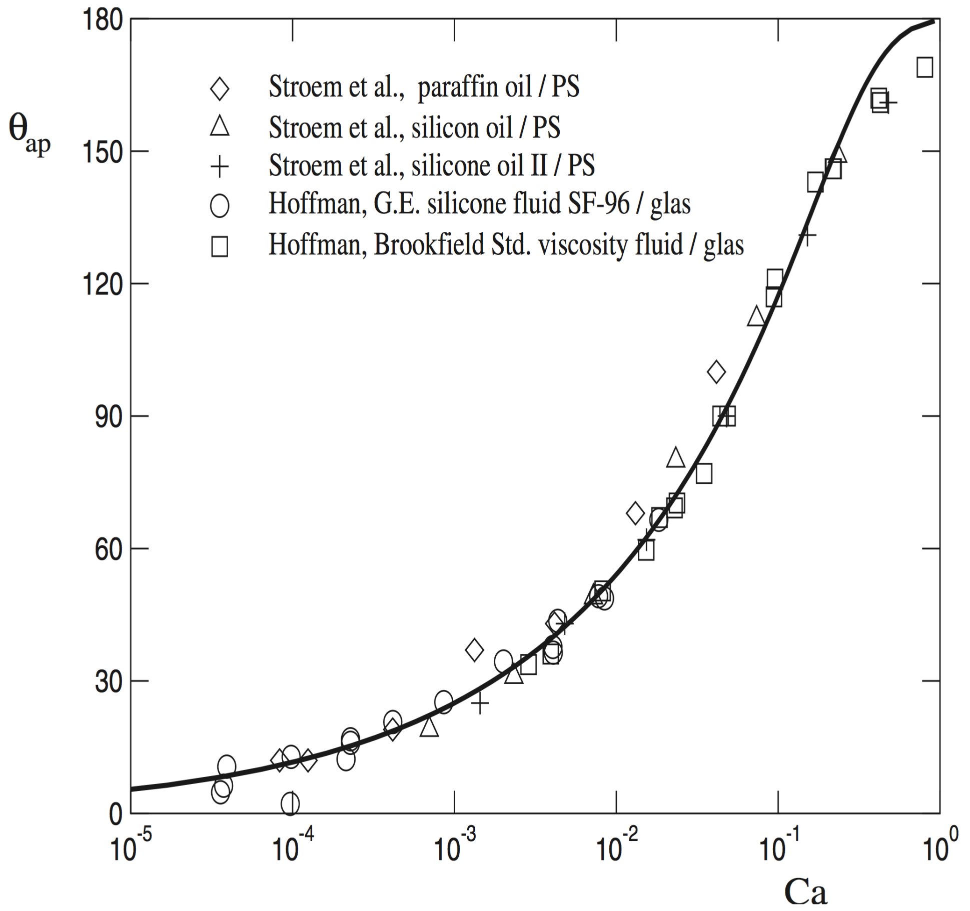
Dynamics of the triple line (Hoffman 1975, Ström et al. 1990)



Adopted from Bonn et al. 2009, Rev. Mod. Phys.

- Apparent dynamic contact angles of perfectly wetting fluids (silicone) measured in a glass capillary (Hoffman, 1975) and for a plunging plate of polystyrene (Ström et al., 1990). Each symbol corresponds to a different fluid and/or substrate.
- One curve for different liquids, conditions.
- For small velocity, the solid line is:

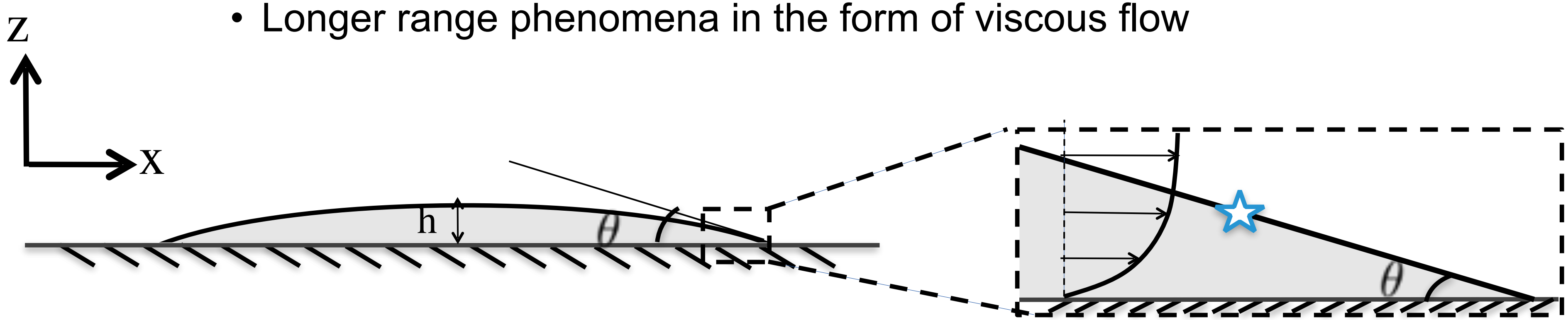
$$\theta_a = \mathrm{const} \cdot \mathrm{Ca}^{1/3}$$

Capillary number $$Ca = \frac{\mu U}{\gamma}$$

Viscous dissipation

The dynamical properties of the contact line involves:

- Local phenomena (molecular scale)
- Longer range phenomena in the form of viscous flow



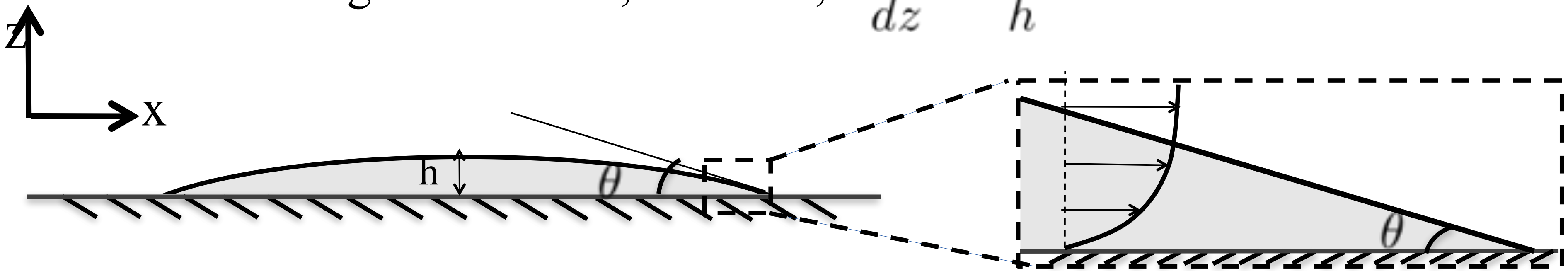
Flow path of markers in the Dussan-Davis experiment (1974). It is similar to the motion of a caterpillar vehicle.

$$T\dot{S} = \int_0^{\infty} dx \int_0^{x\theta_D} \eta \left(\frac{dv}{dz}\right)^2 dz$$

The energy dissipated by viscous flow
(per unit length of the triple line in the y-direction)

Deriving laws for dynamic wetting: Hydrodynamics

- Assume a wedge with $\theta << 1, \;\; h = \theta x, \;\; \frac{du}{dz} \approx \frac{V}{h}$



- Energy dissipated by viscous phenomena (becomes logarithmically divergent)

$$T\dot{S} = \int_0^\infty dx \int_0^h \mu \left(\frac{du}{dz}\right)^2 dz \approx \frac{\mu V^2}{\theta} \int_0^\infty \frac{dx}{x}$$

- This implies that the total dissipation is not integrable at r = 0 nor at ∞, and one requires a cutoff at both small and large scales. Typically, these cutoffs appear at the molecular scale (a~10^{-9} m) and at the scale of the capillary length L (~10^{-3} m).

$$\int_0^\infty \frac{dx}{x} \approx \int_a^L \frac{dx}{x} = \ln\left(\frac{L}{a}\right) \equiv l$$

Viscous dissipation in Hoffmann's exp.

- From: $$F(\theta_D) = \gamma_{SG} - \gamma_{SL} - \gamma \cos\theta_D$$

$$T\dot{S} = FV = \frac{3\eta l}{\theta_D} V^2$$

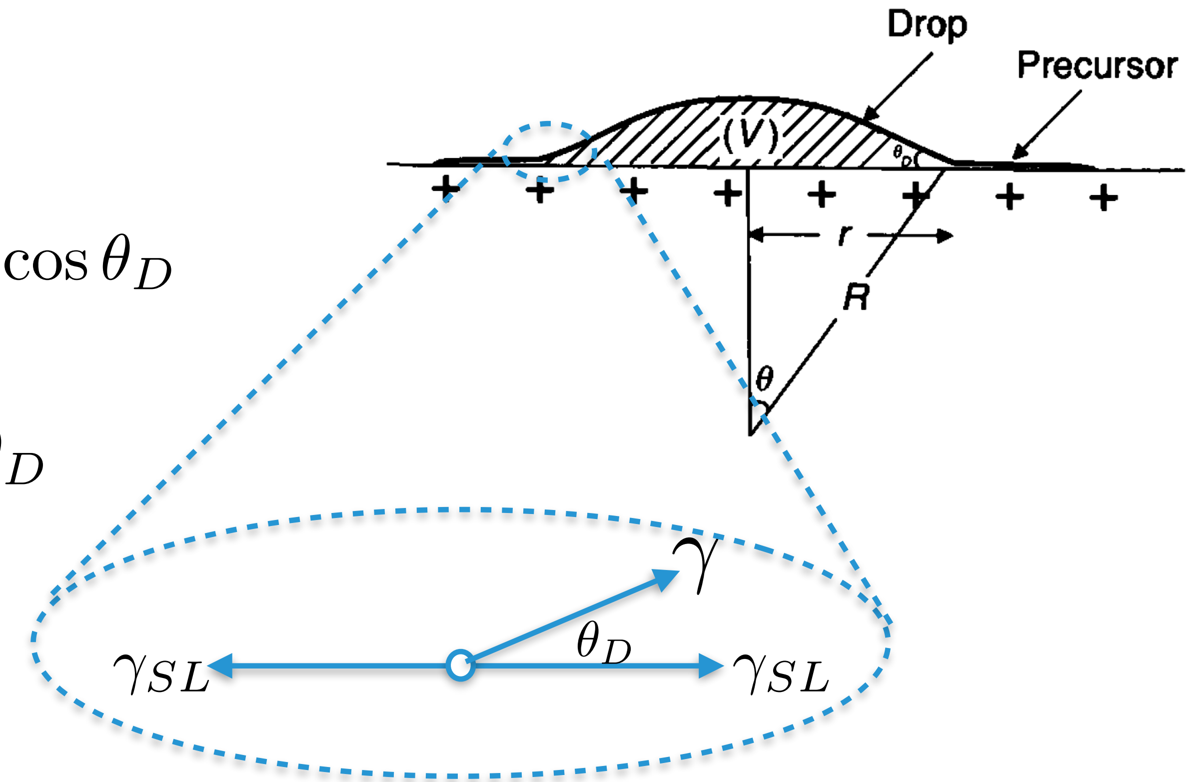
$$\cos\theta \approx 1 - \frac{\theta^2}{2}$$

- We have: $$V = \left(\frac{\gamma}{\eta}\right) \frac{\theta_D}{6l} (\theta_D^2 - \theta_E^2)$$

$$Ca = const \cdot \theta_D^3$$

- + When $\theta_D = \theta_E$, V=0

Tanner's law (1979) – perfect wetting



General case:

$$F(\theta_D) = \gamma_{SG} - \gamma_{SL} - \gamma\cos\theta_D$$

Total wetting case:

$$F_{inside} = -\gamma_{SL} - \gamma\cos\theta_D$$

$$F_{precursor} = \gamma_{SL} + \gamma$$

$$\Rightarrow \quad \tilde{F} = \gamma - \gamma\cos\theta_D \cong \gamma\frac{\theta_D^2}{2}$$

Predict the velocity through the dissipation equation ($T\dot{S} = FV$), with the new F:

$$V = \frac{V^*}{6l}\theta_D^3$$

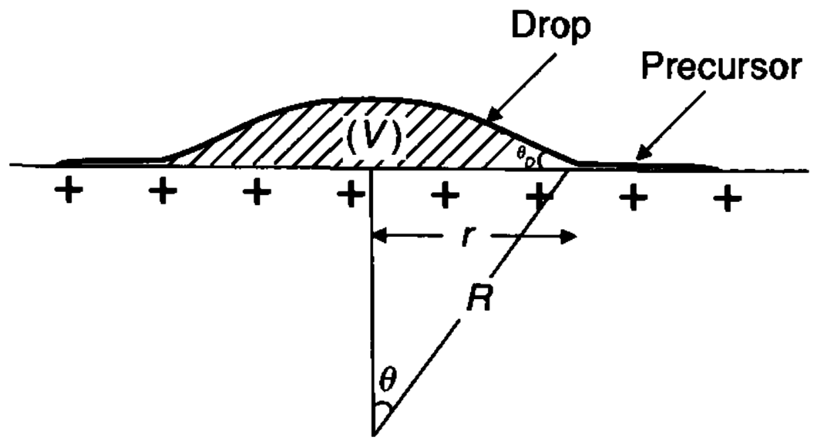
Tanner's law (1979) – perfect wetting

Geometry: assuming the drop is sufficiently flat.

$$h(r) = \frac{2\Omega}{\pi R^2}\left[1-\left(\frac{r}{R}\right)^2\right] \Rightarrow h'(r) = -\frac{4r\Omega}{\pi R^4}$$

but, $-h'(R) = tan(\theta_D) \approx \theta_D$

$$\Rightarrow \Omega = \frac{\pi}{4}R^3\theta_D$$



Due to the mass conservative, $d\Omega/dt = 0$, and $V=f(\theta_D^3)$

$$\Rightarrow \quad \frac{d\theta_D}{dt} = -\frac{V^*}{R}\theta_D^4$$

Recast from the initial size of the droplet, $L \approx \Omega^{1/3}$

$$\frac{d\theta_D}{dt} = -\frac{V^*}{L}\theta_D^{13/3} \quad \Rightarrow \quad \theta_D \approx \left(\frac{\mu L}{\gamma t}\right)^{3/10}$$

$$R \propto \left(\frac{\gamma t}{\mu L}\right)^{1/10}$$

Cox law (1986)

- Assuming the curvature of the outer region is small, and the bulk viscous friction is the main resistance force.
- Assuming the slippage of fluid occurs in the inner region.

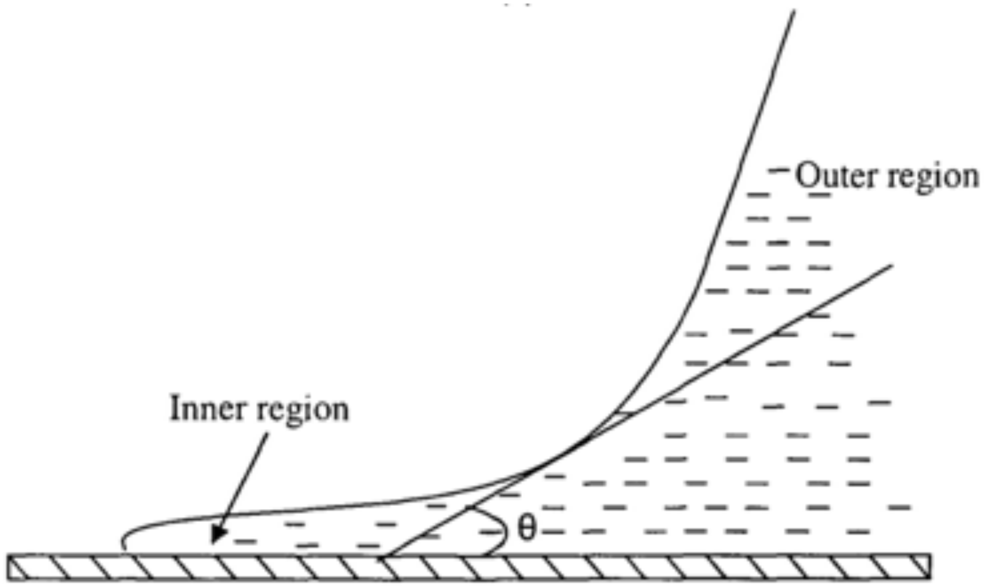
$$g(\theta_d) = g(\theta_{eq}) + Ca \ln\left(\frac{L}{l}\right)$$

for a solid/liquid/gas system,
$g(\theta) = \theta^3/9$, thus

$$\theta_d^3 = \theta_{eq}^3 + 9Ca \ln\left(\frac{L}{l}\right)$$

L is the capillary length,
and l is the slip length.

(*What happen if $l \sim 0$?*)



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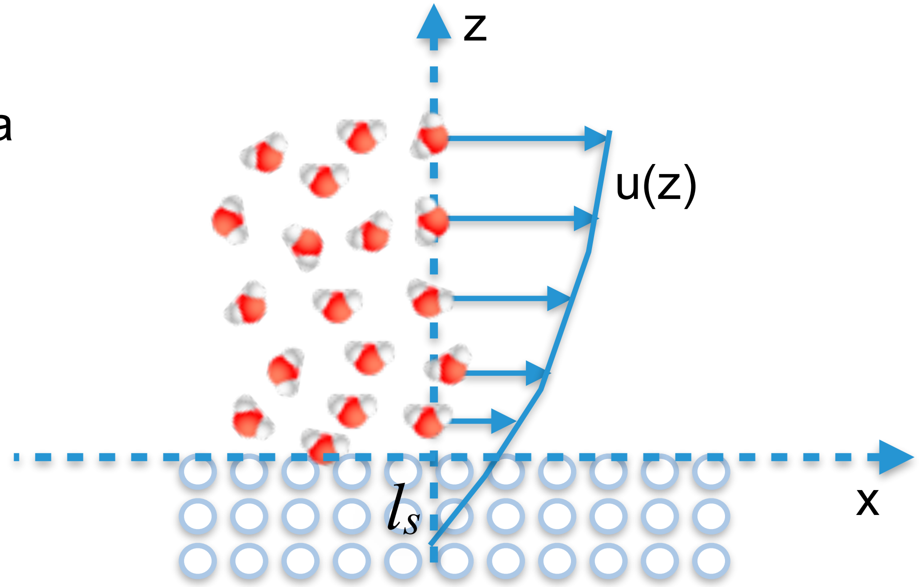
Summary

- Statics problems
  - Hydrodynamics: forces, velocity, stress and singular flow in the vicinity of the interface.
  - Thermodynamics: Gibbs free energy and equilibrium contact angle
  - Physicochemical interaction: surfactant and surface tension
  - Evaporation, electrowetting etc.
- Dynamics wetting
  - Dynamics wetting contact angle theories: dissipation energy
  - Microscopic model: molecular kinetic theory
  - Numerical model: free energy based

Microscopic model: slip length

The motion of the first few molecular layers above a solid subtract can be described by the Navier slip boundary.

$$u_{z=0} = l_s \frac{\partial u(z)}{\partial z}$$



(*) For gas, l_s ~ the mean free path (Maxwell 1878)

(*) For liquids,

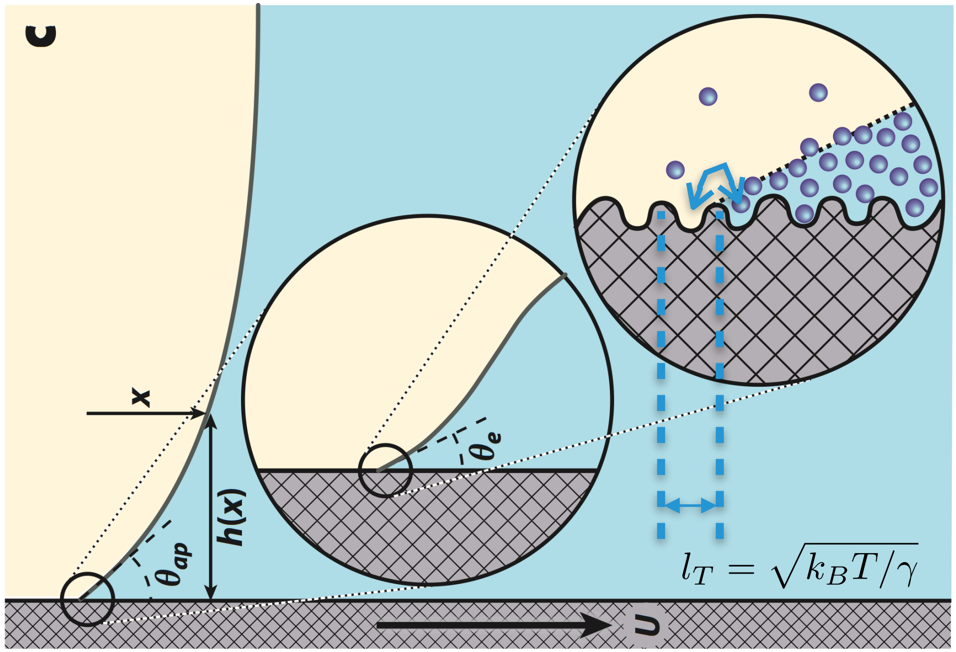
$$l_s \sim \frac{\eta D a k_B T}{[\gamma a^2(1+\cos\theta_e)]^2} a$$

(Huang et al. 2008)

a is the molecular size, D is the self-diffusion coefficient, $\gamma(1+\cos\theta)$ is the wettability factor

Microscopic model: Molecular Kinetic Theory

- The key idea of this MKT is that a contact line moves by small jumps included by thermal fluctuations.
- The "jump" motion is characterised by a length scale ξ and by an energy barrier for the active process $E^* \sim \gamma\xi^2(1+\cos\theta_e)$ (Blake 2006).
- Average moving velocity



$$U = 2k_0\xi \exp\left(-\frac{E^*}{k_B T}\right) \sinh\left(\frac{\gamma\xi^2(\cos\theta_e - \cos\theta)}{2k_B T}\right)$$

where, k_0 is the typical "jump" frequency, k_B is Boltzmann constant, $\gamma\xi(\cos\theta_e - \cos\theta)$ is the capillary force.

- The current model does not represent any contact angle hysteresis.

Linearized Molecular Kinetic Theory

- The original form

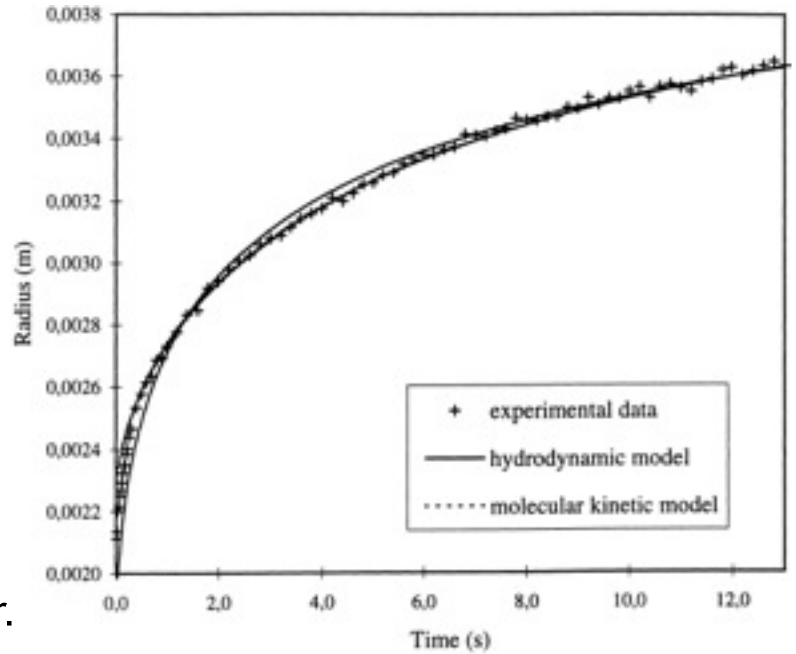
$$U = 2k_0\xi \exp\left(-\frac{E^*}{k_BT}\right)\sinh\left(\frac{\gamma\xi^2(\cos\theta_e - \cos\theta)}{2k_BT}\right)$$

$$\frac{\gamma\xi^2}{k_BT} = (\xi/l_T)^2 = \mathcal{O}(1) \quad \Rightarrow \quad \sinh\left(\frac{\gamma\xi^2(\cos\theta_e - \cos\theta)}{2k_BT}\right) \approx (\cos\theta_e - \cos\theta)$$

- Combining with the Eyring viscosity we have U_{MKT},

$$U_{MKT} = \frac{\gamma}{\nu}\exp\left(\frac{E_\nu - E^*}{k_BT}\right)(\cos\theta_e - \cos\theta)$$

E_ν is the activation energy from liquid-liquid interactions, $E_\nu \sim 2\gamma\xi^2$



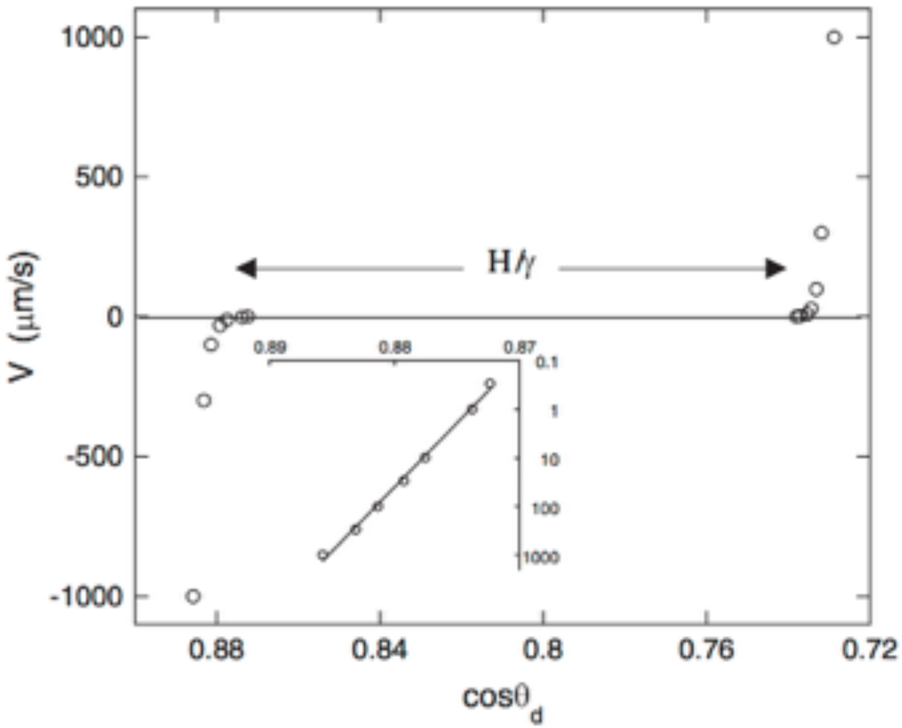
de Ruijter et al.,*1999, Langmuir*.

Microscopic model: surface heterogeneities

- The heterogeneities can be modelled by considered the “jump” of the molecular as depinning events from the defects of the substrate. In this picture, the length scale ξ is now the correlation length of the disorder and *E** the typical energy barrier between two pinned configurations of the contact line.

$$U \simeq 2k_0\xi \exp\left(-\frac{\xi^2}{l_T^2}H\right)\exp|\cos\theta_e - \cos\theta|$$

where H is the contact hysteresis,
$H=1/2(\cos\theta_r-\cos\theta_a)$



E. Rolley, PRL 2007

Short summary for the dynamic wetting models

- Both hydrodynamic and molecular kinetic theory rely on primary input from the micro scale

- Both theories have been shown to describe experimental data.

- Experiments of short-time spontaneous spreading of drops are however difficult to describe with either theory.

- <u>Aim here to </u>develop a modeling approach for dynamic wetting, going beyond function fitting.

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Transition of fluid flow due to the wetting the capillary forces

KTH
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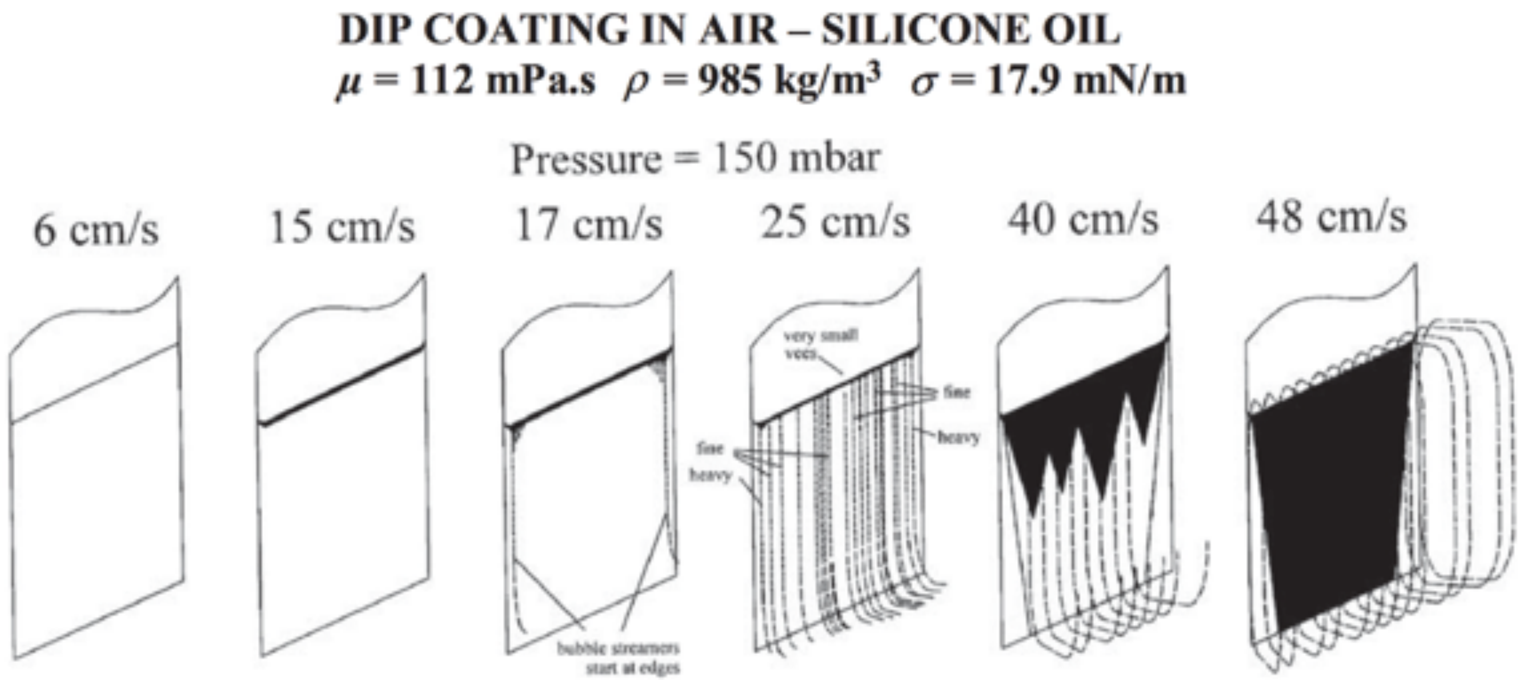
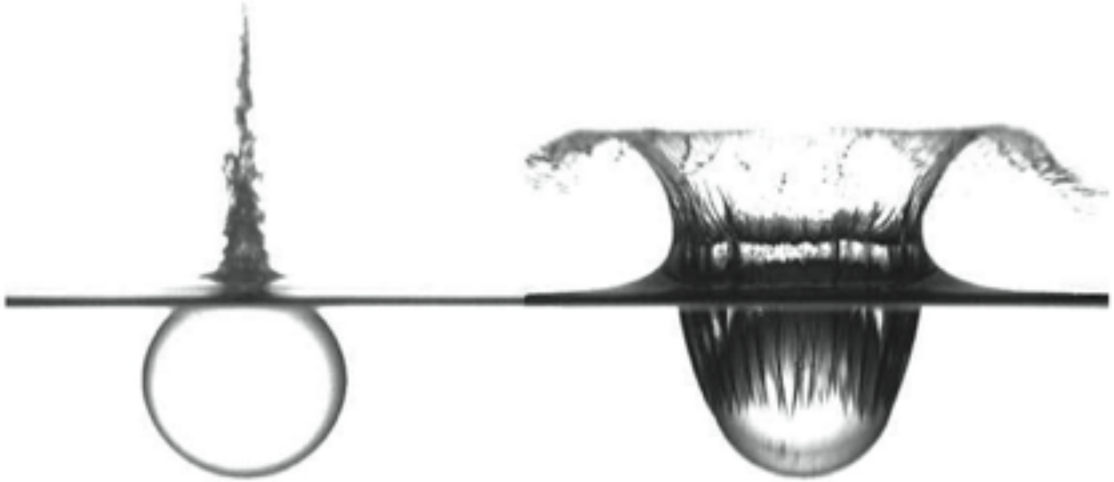
Motivation

- For many practical applications such as coating, it is important to understand the maximum speed at which a plate withdrawn or plunging into a liquid is covered exclusively by one phase.

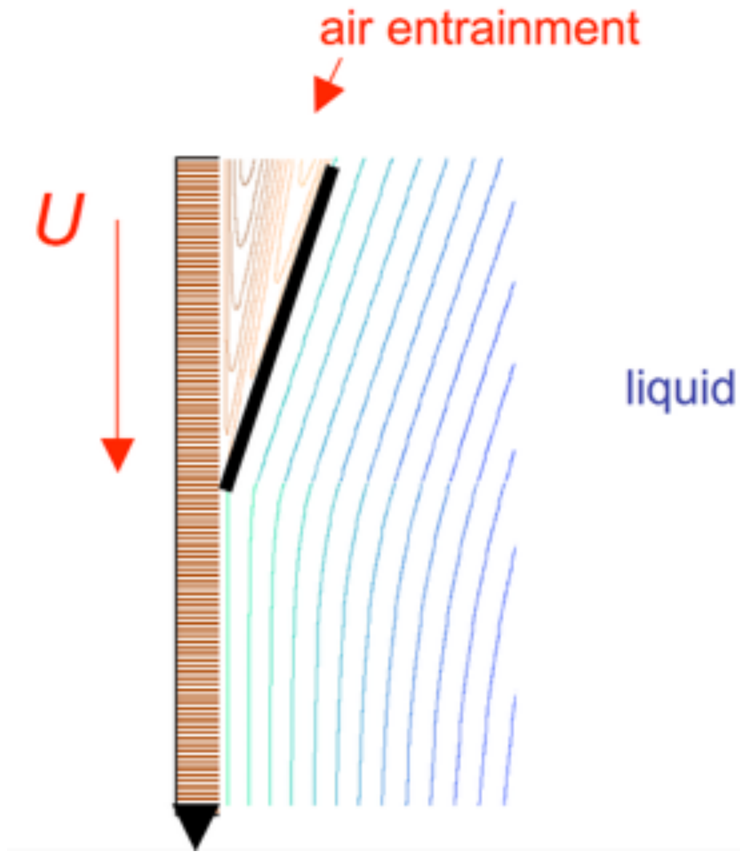


Benkreira & Ikin 2010

Flow transition: slip to splash



The splash produced by a sphere impacting on water is caused by the contact line of the solid-air-water interface becoming unstable, so a sheet of water detaches from the solid. On the left, no instability occurs for a static contact angle of $\theta_{eq}=15^o$, while for $\theta_{eq}=100^o$ a splash is produced.



The entrainment of air occurs at much larger speeds than the dynamical wetting transition for receding contact lines.

Ca and equilibrium contact angle determine the splash

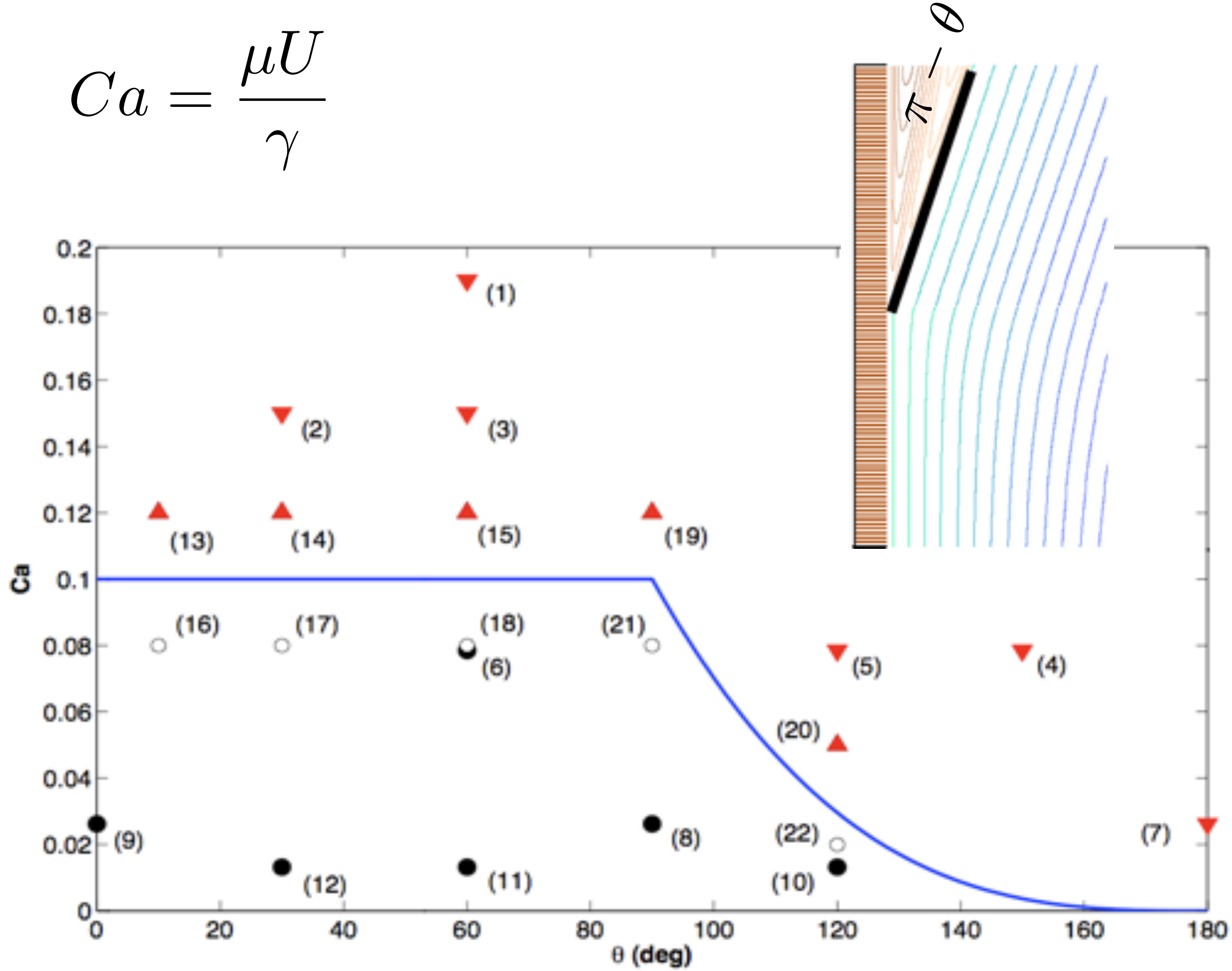
$$Ca = \frac{\mu U}{\gamma}$$

The blue curve condenses the theoretical/experimental results of Duez et al:

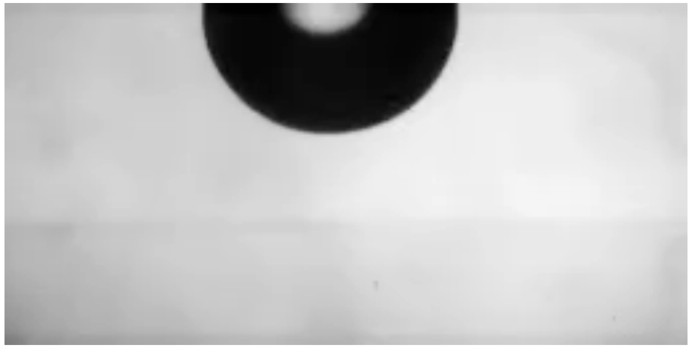
Hydrophilic (theta<90˚):
Ca > 0.1 gives splash

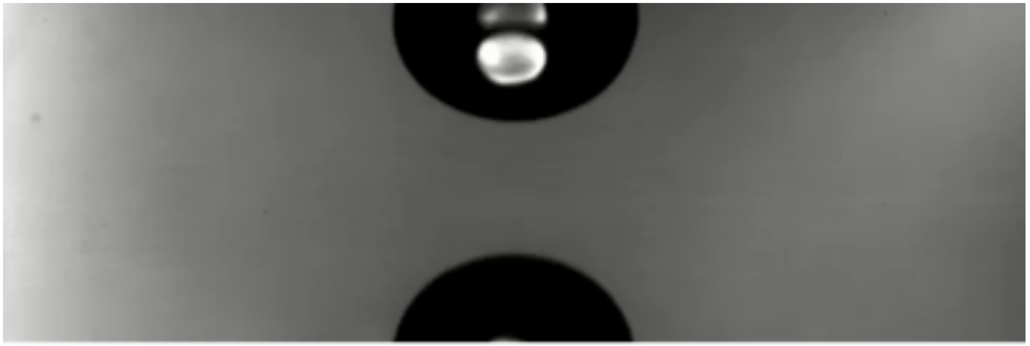
Hydrophobic (theta>90˚):
Ca ~ $(\pi-\theta)^3$

Splash above the curve, slip below.



Ca vs. viscosity: A drop of ethanol & silicon impact a dry surface



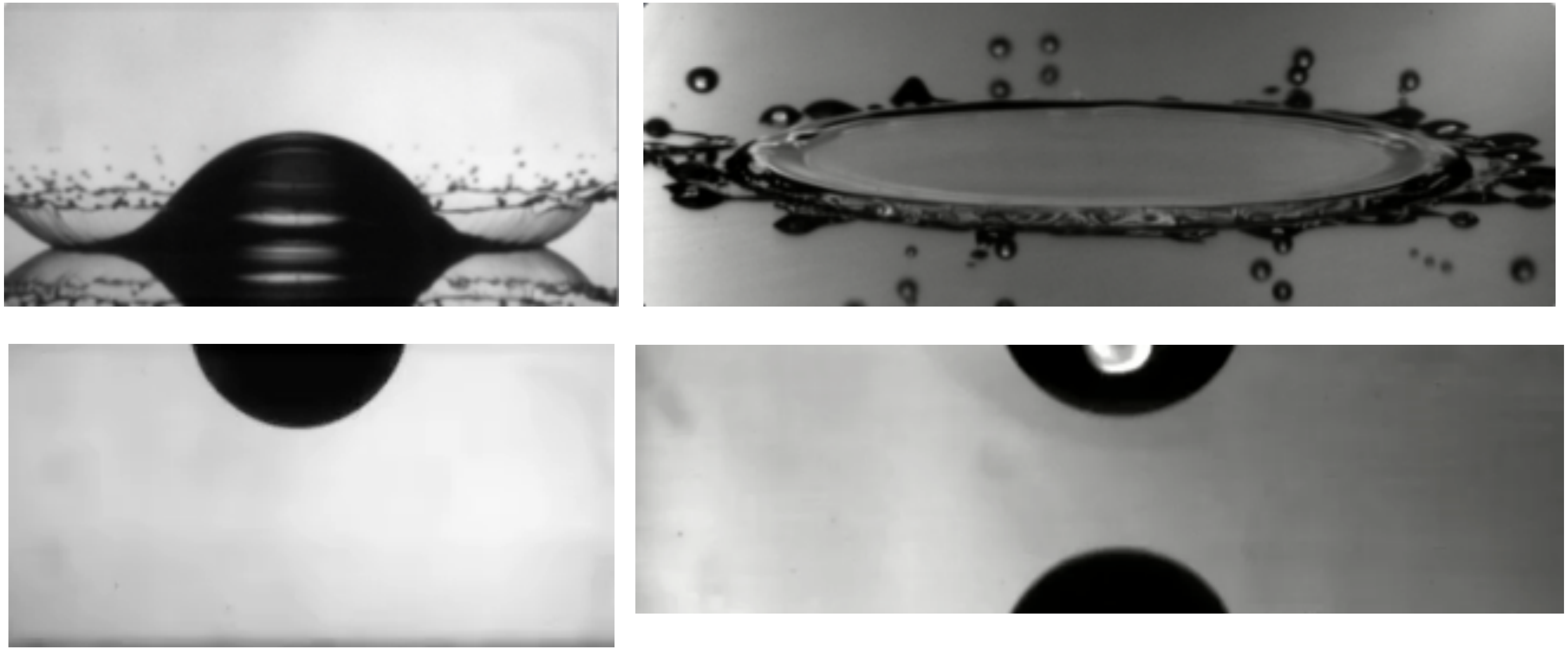


1atm

Nagel Group, Chicago Univ.

- The critical speed decreases for more vicious liquids, suggesting that dissipation in the liquid is importance. (Benkreira & Ikin 2010, Blake & Ruschak 1979)
- The dependence on η_l is much weaker than predicted (Cox $1/\eta_l$); in between $-1/2$ and $-1/3$ rather than the expected -1.

Ca vs. gas pressure: A drop of ethanol & silicon impact a dry surface



1 atm

0.2 atm

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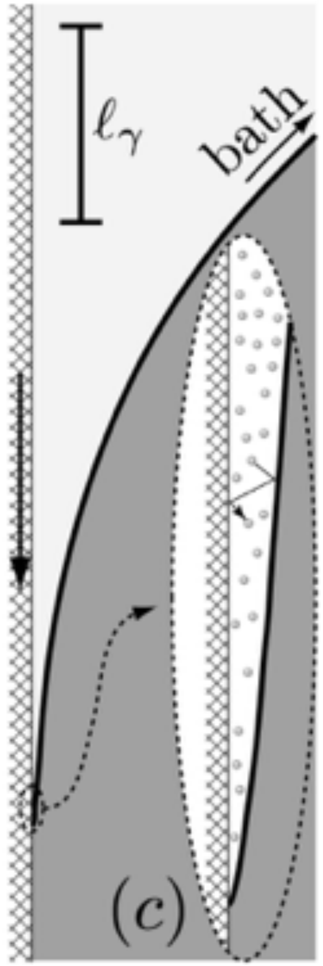
- The critical speed increases when the air pressure is reduced. Because such a pressure change does not affect the gas viscosity, this effect must result from inertia in the gas or from the increase of the mean free path.

Ca vs. gas pressure

- A pressure reduction does not affect the dynamical viscosity of a gas (Lemmon 2004), but it does increase the mean free path by a factor p_{atm}/p.
- Under atmospheric conditions l_{mfp}≈70 nm, the mean free path is pushed well into the micron range when pressure is reduced by a factor 100.
- The mean free path then becomes comparable to the film thickness measured experimentally.
- Since l_{mfp} sets the scale for the slip length, we expect a substantial reduction of dissipation in the gas, and hence a larger entrainment velocity. Then increase of Ca.



(Marchand et al. 2012)

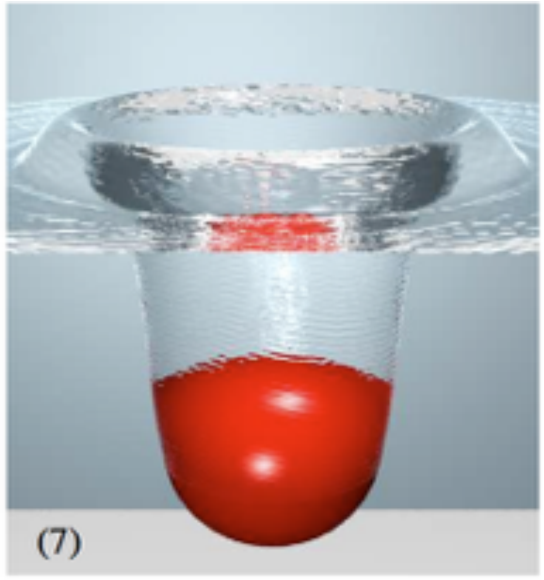
Simulations

Cahn Hilliard equations
Axisymmetry
Adaptive FEM

Computations done in a frame following the ball
Ball speed assumed constant, prescribed

Data typically for water/air, bead diameter 0.83 mm, speed U=6 m/s. Surface energies are varied.

Most relevant nondimensional numbers:

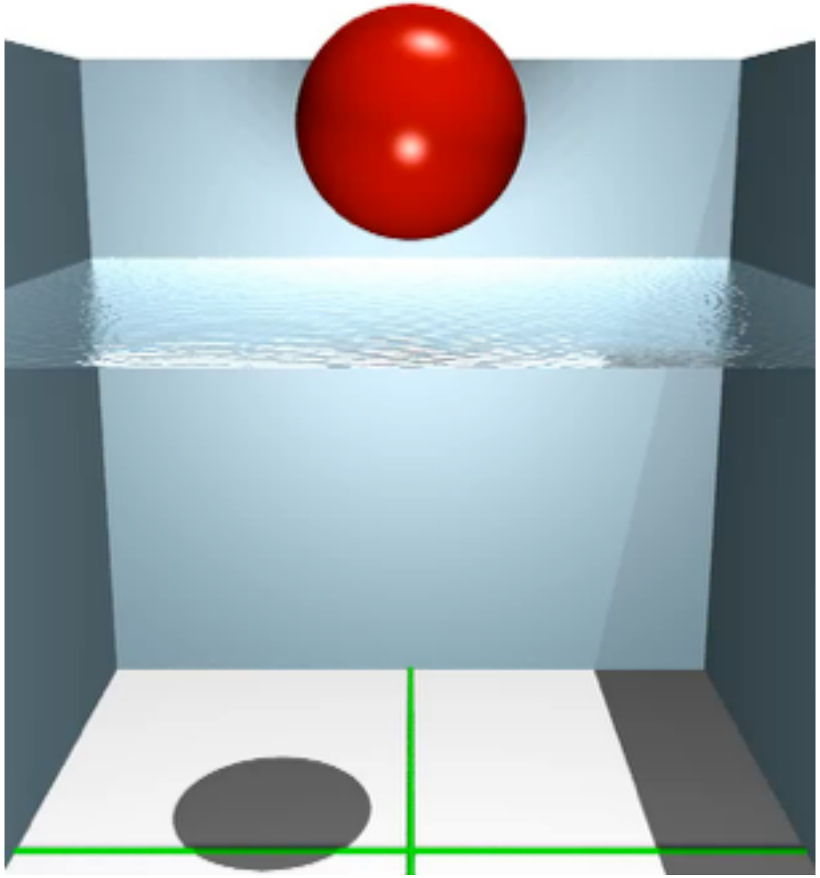


Do-Quang and Amberg, *Phys. Fluids* (2009)

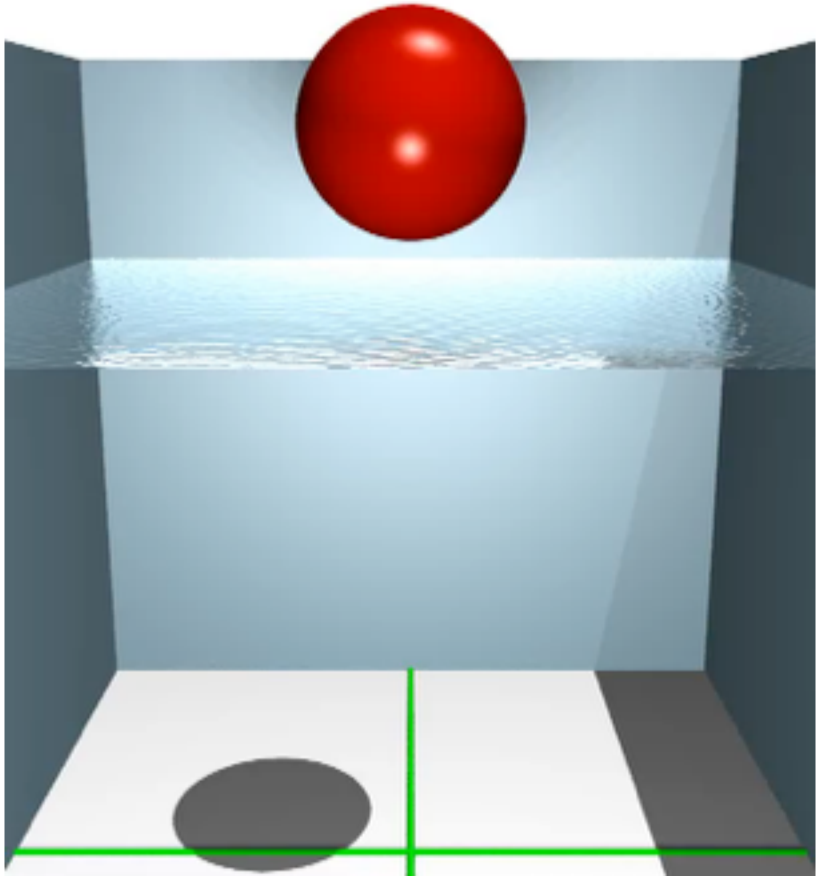
$$Ca = \frac{\mu_l U}{\gamma_{gl}}, \quad \mathrm{Re} = \frac{\rho_l U d}{\mu_l}, \quad Bo = \frac{(\rho_l - \rho_a) g d^2}{\gamma_{gl}}$$

Typical values for the simulations:
Ca= 0.0785, Re = 5000, Bo=0.092

Ball impacting a free water surface



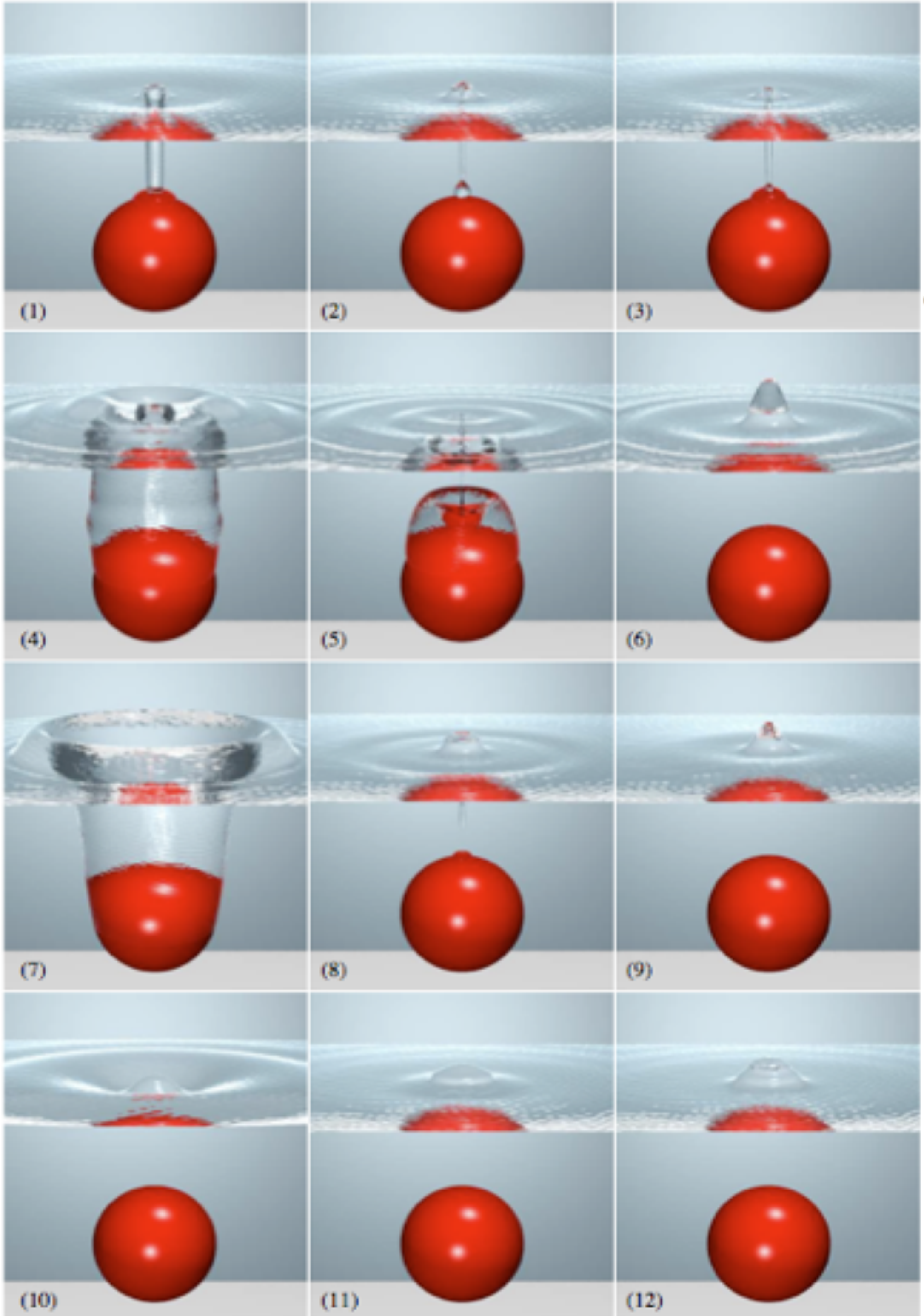
Contact angle of ball is 60^o

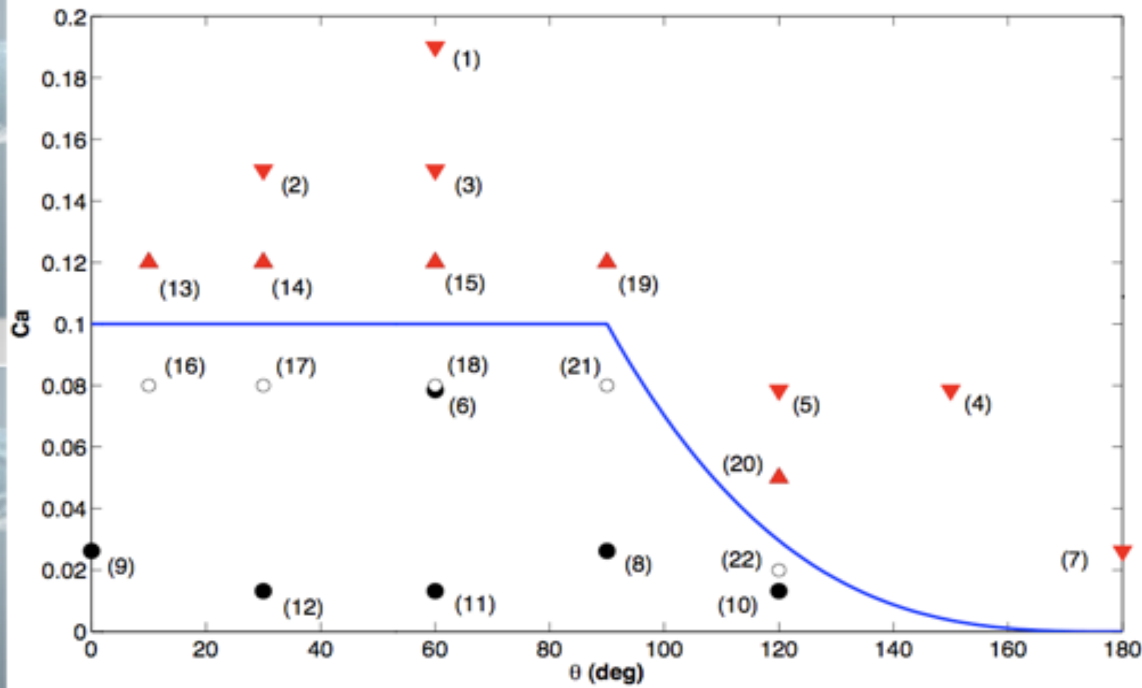


Contact angle of ball is 150^o

Falling speed U=5m/s

(Do-Quang, *Phys. Fluids* (2009))

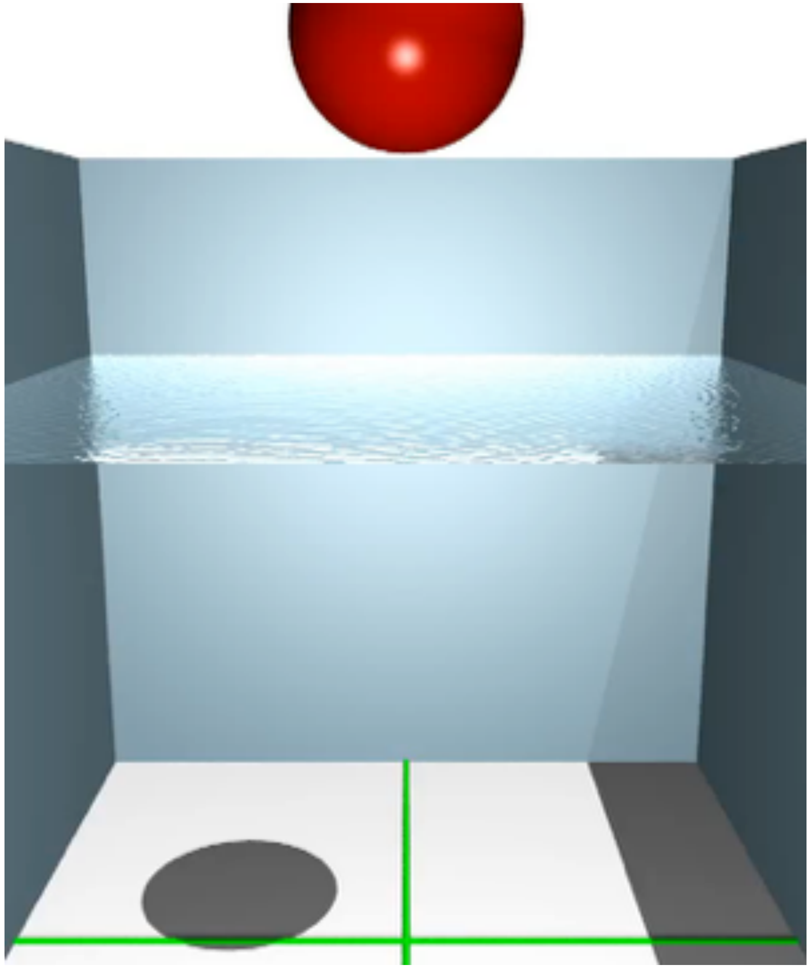




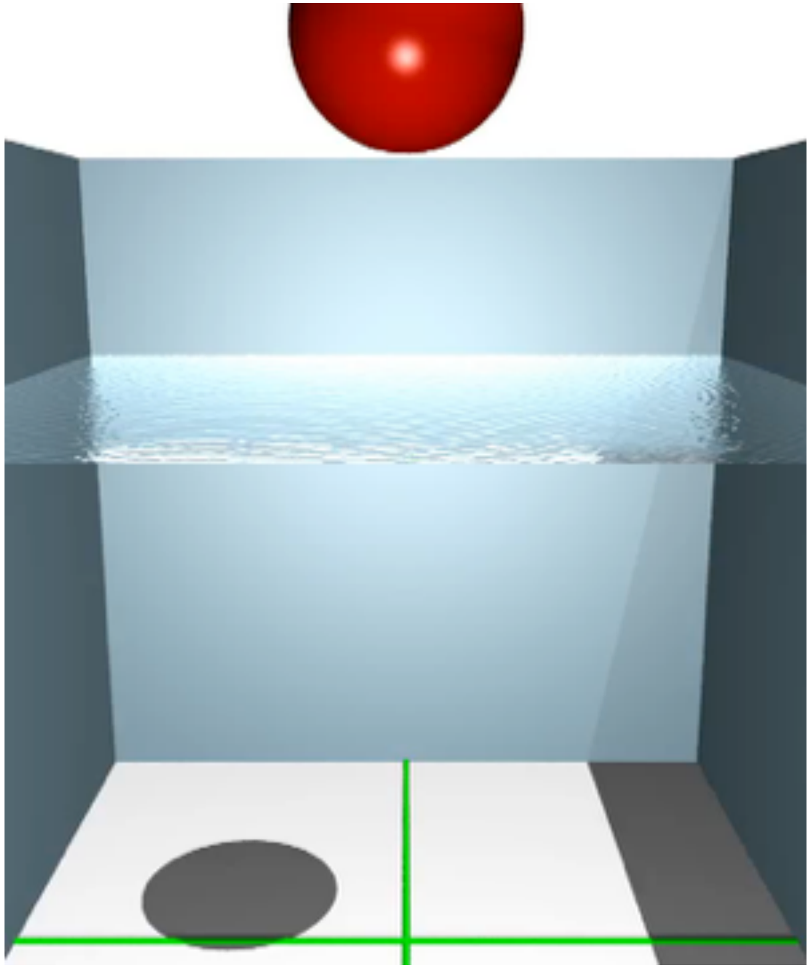
Symbols are our simulations
Red: Air cavity still exists
Black: No coherent air cavity

Same *Ca* as in experiments
Bo < 1 (*Bo* >1 in exps)
Re~1000 (*Re*~10000 in exps)

Bouncing ball



$\theta=90^\circ$



$\theta=150^\circ$

Notice

- Detailed simulations of a highly dynamic wetting situation.

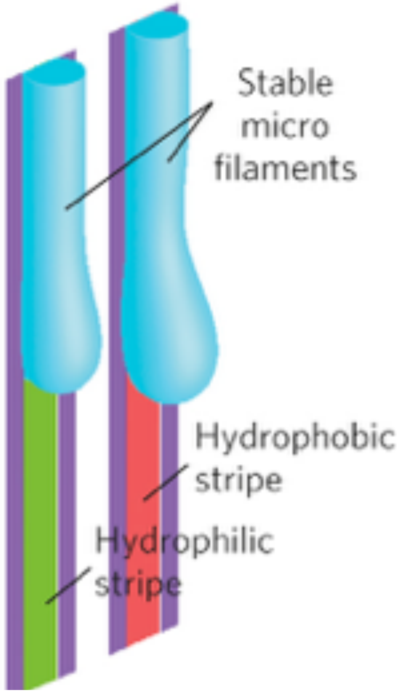
- Agreement with experimental results;

- Agreement despite large differences in Bond and Reynolds numbers: suggests that the important factors here are dynamic wetting and inertia.

Controlled drop emission by wetting properties

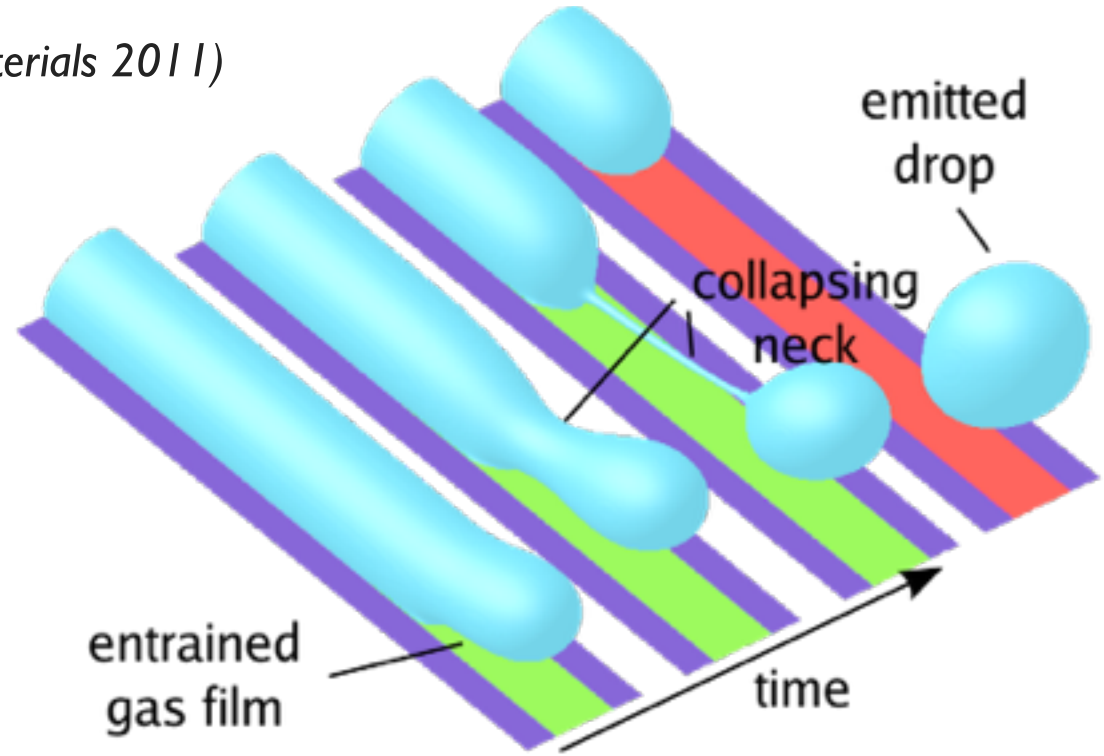
- An instability induced by the competition between capillarity, viscous dissipation and <u>wetting</u>, which leads to the controlled generation of drops by appropriately tuning the wetting properties of the solid substrate.

(Ledesma-Aguilar, R. et al, Natural Materials 2011)



$\theta_e = 0^\circ, Ca = 0.41$

$\theta_e = 90^\circ, Ca = 0.25$



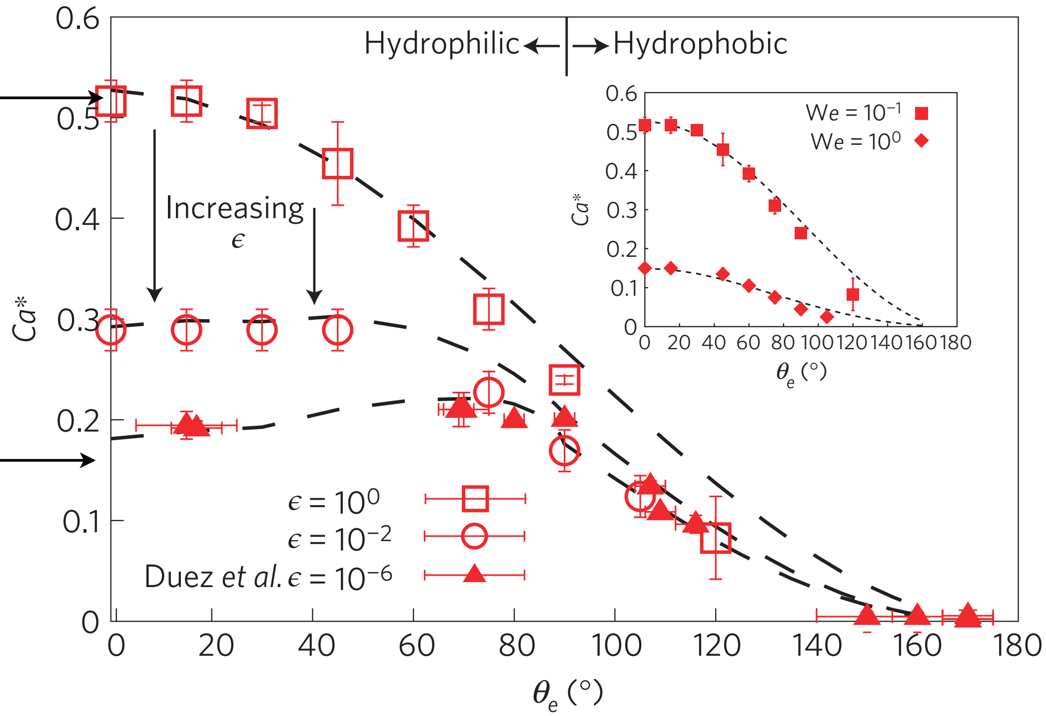
$\theta_e = 0^\circ, Ca > Ca^* = 0.52$

$\theta_e = 90^\circ, Ca > Ca^* = 0.27$

Controlled drop emission by wetting properties

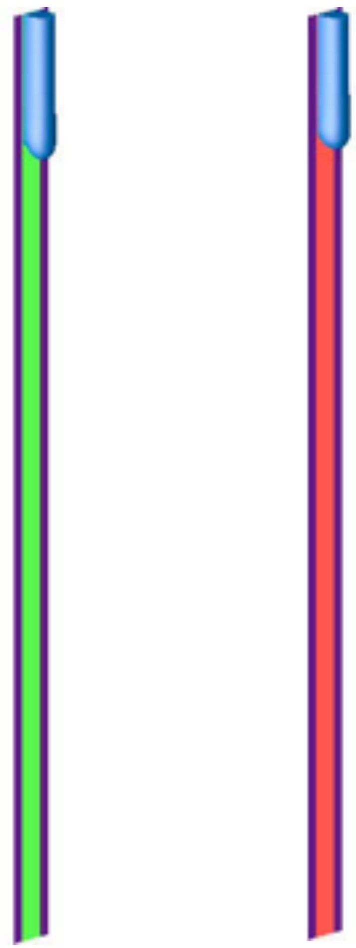
A complex fluids with small surface tension, such as colloid/polymer mixtures

Water



Critical capillary number, Ca^* , as a function of the static contact angle, θ_e, at different values of the length-scale-separation parameter, $\varepsilon=\xi/h$. Ca^*. Symbols correspond to simulations (squares and circles) and experimental data (triangles). Dashed lines correspond to the theoretical prediction as a result of the global energy balance per unit length of the contact line between the power generated by driving forces and the dissipation due to frictional forces.

(Ledesma-Aguilar, R. et al, Natural Materials 2011)

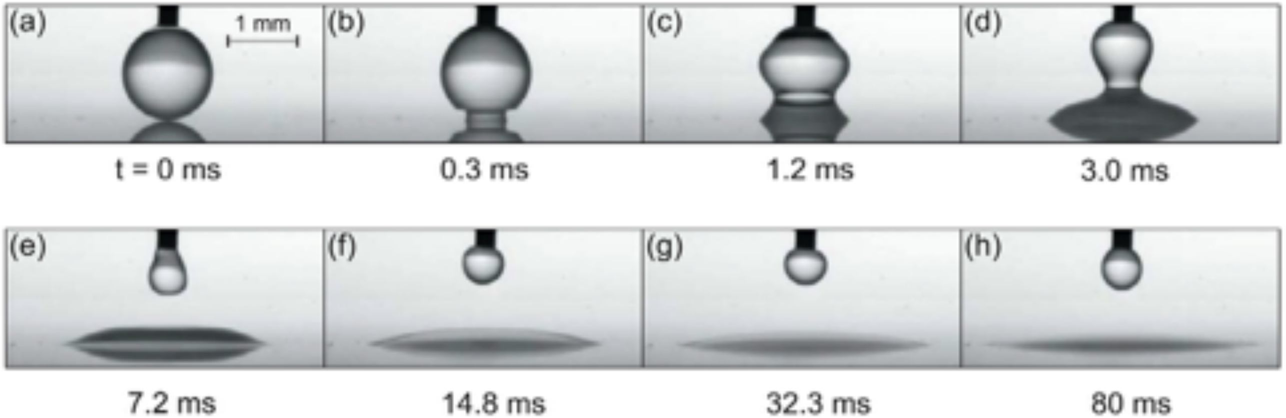


$\theta_e = 0^\circ, Ca > Ca^* = 0.52$

$\theta_e = 90^\circ, Ca > Ca^* = 0.27$

LINNÉ FLOW CENTRE

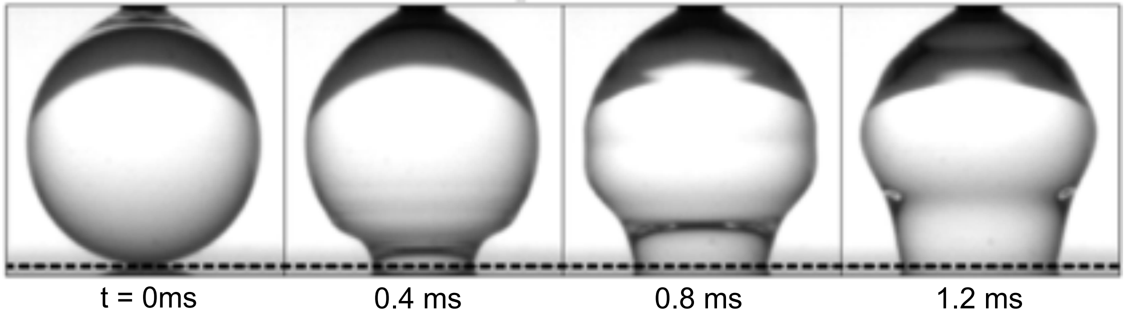
Spontaneous droplet spreading



θ=3°

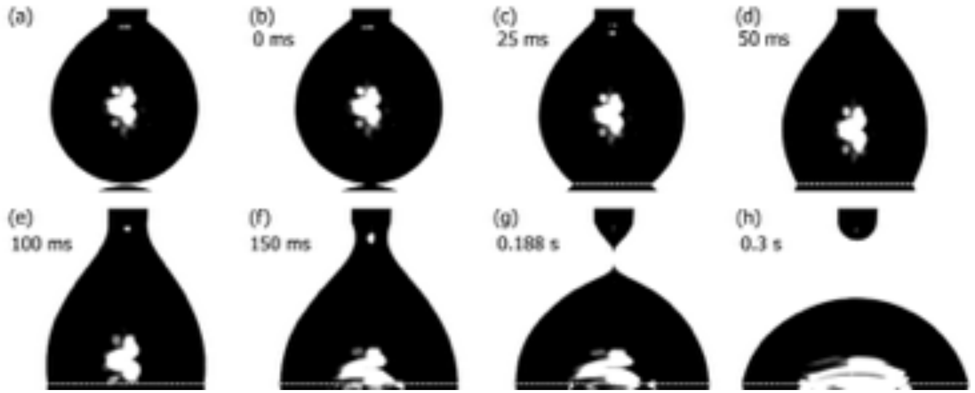
Courbin et al., PCM, 2009.

θ=43°



Bird et al., PRL, 2008.

Glycerol droplet, θ=53°



Bliznyuk et al., Langmuir, 2010.

Time scale definition

- If the capillary forces driving the flow are primarily hindered by viscosity

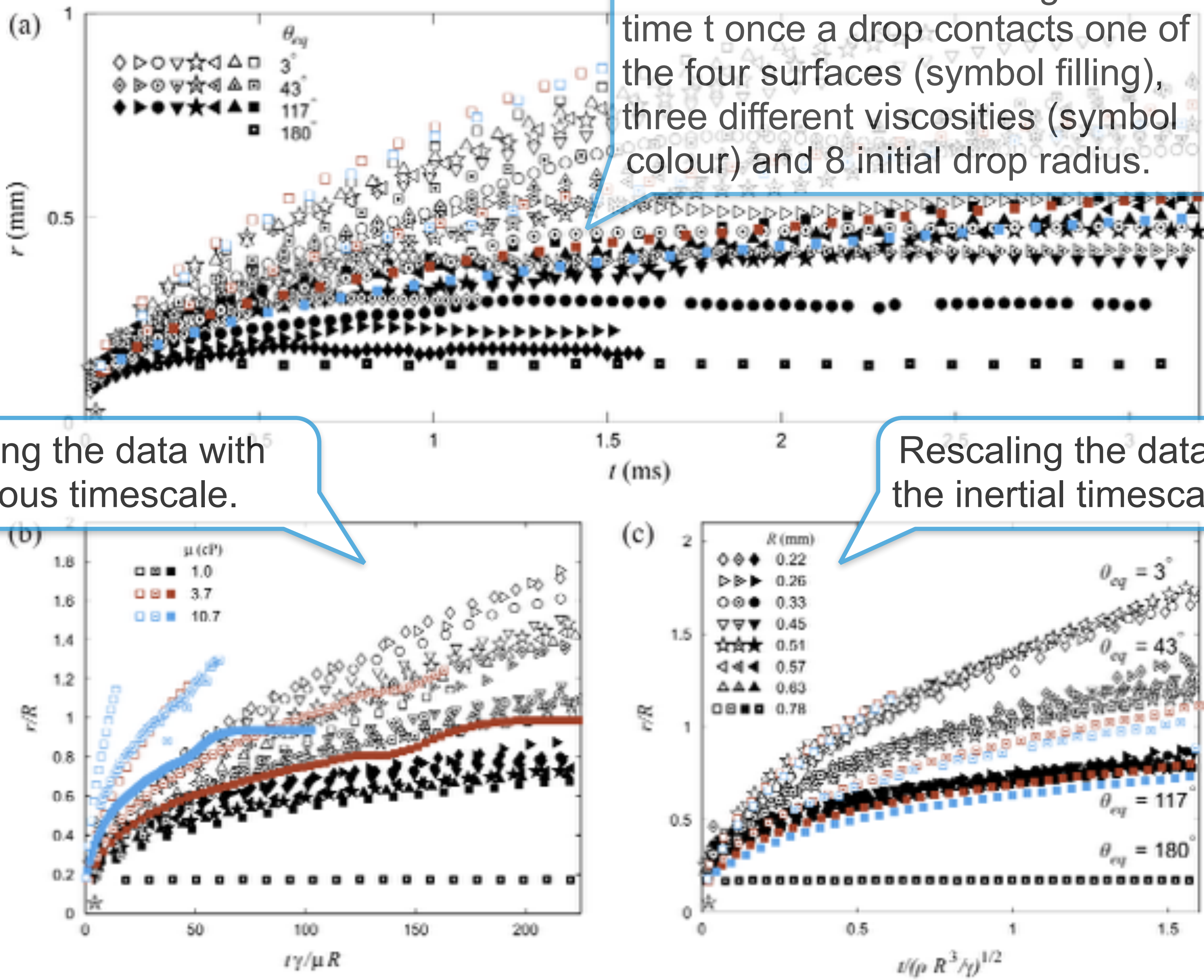
$$t^* = \frac{\mu R}{\gamma} \qquad \frac{[N.s/m^2].[m]}{[N/m]} = [s]$$

- If the capillary forces driving the flow are primarily hindered by inertia, based on density ρ and surface tension

$$t^* = \sqrt{\frac{\rho R^3}{\gamma}} \qquad \frac{[kg.m^{-3}] \cdot [m^3]}{[N/m]} = \frac{[kg]}{[kg.m.s^{-2}/m]} = [s^2]$$

Spreading radius of droplets

How the wetted radius r grows with time t once a drop contacts one of the four surfaces (symbol filling), three different viscosities (symbol colour) and 8 initial drop radius.



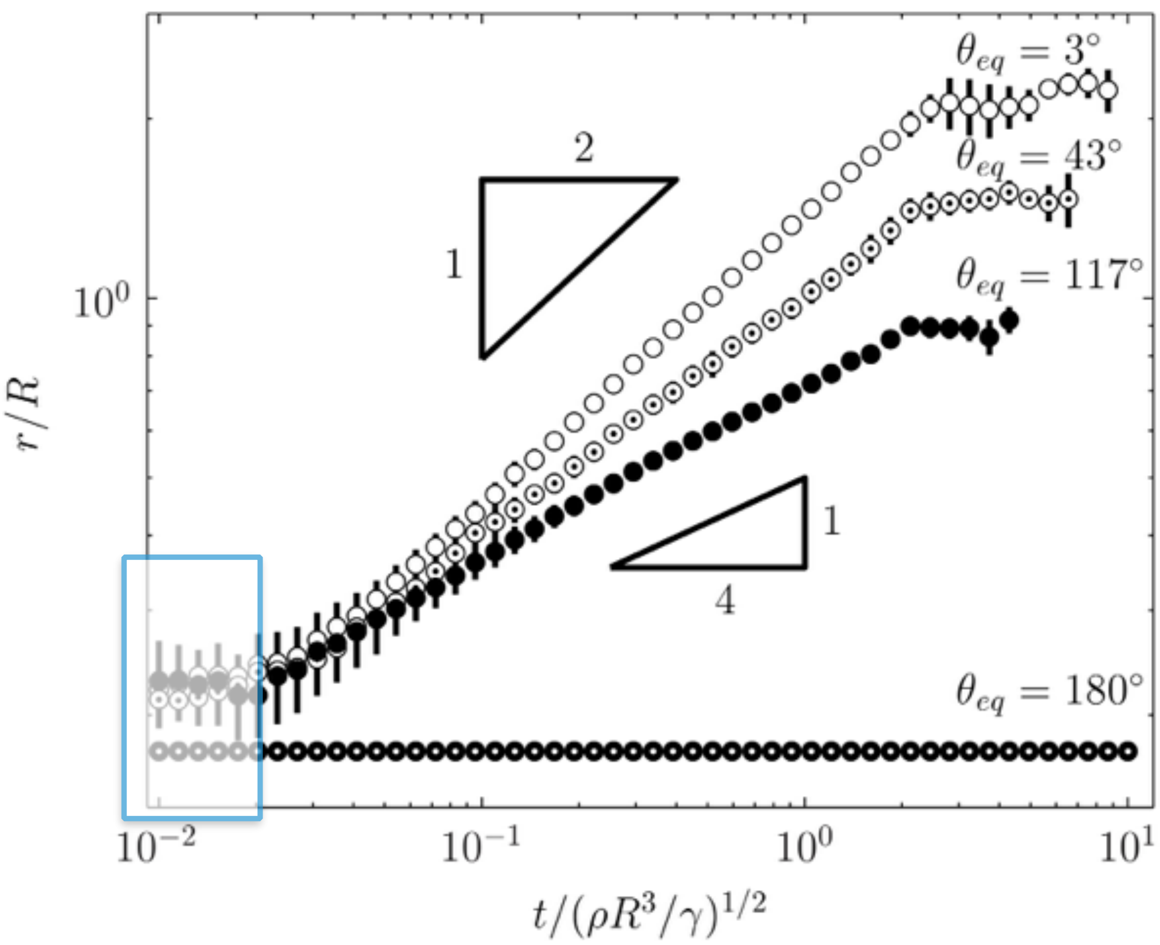
Rescaling the data with the viscous timescale.

Rescaling the data with the inertial timescale.

LINNÉ FLOW CENTRE

Bird et al., PRL, 2008.

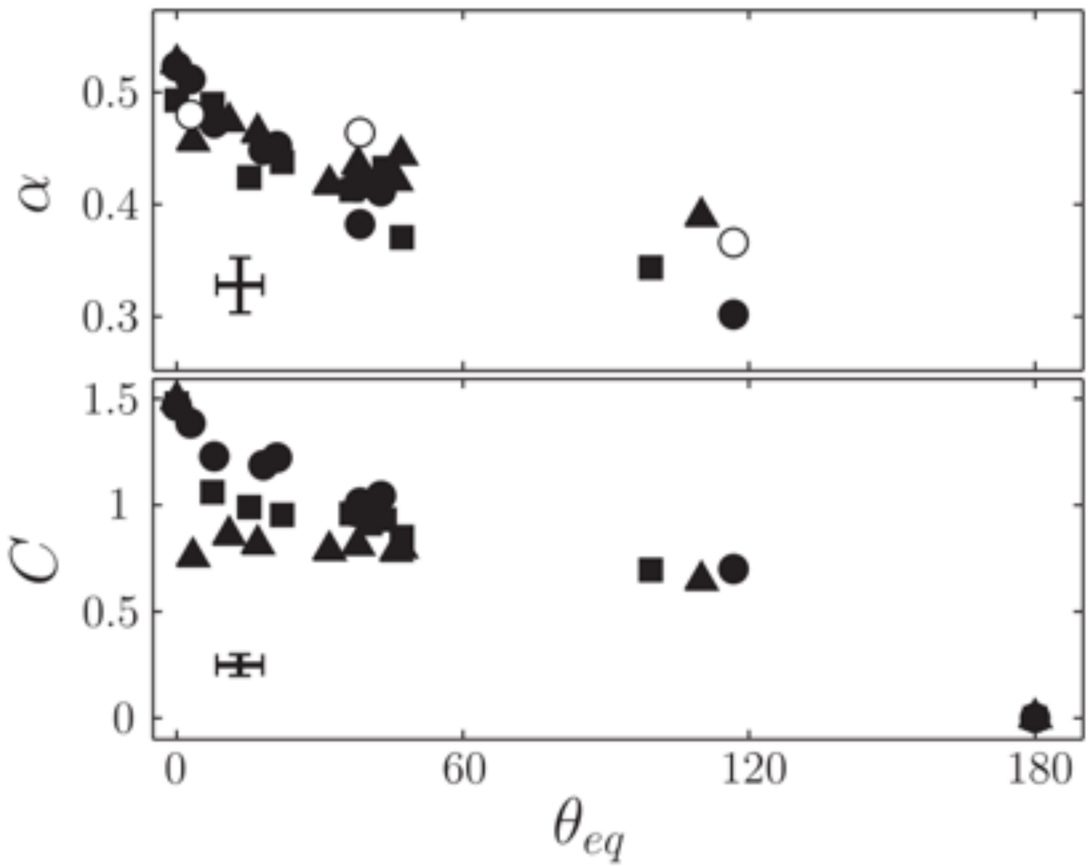
Depends on the equilibrium contact angles



$$\frac{r}{R} = C\left(\frac{t}{\tau}\right)^{\alpha}$$

For small contact angle, α approaches 1/2, a values observed for complete wetting and coalescence.

$$\frac{r}{R} = C\left(\frac{t}{\tau}\right)^{\alpha}$$



As the equilibrium contact angle, θ_{eq} increases, both the coefficient C and the exponent α decrease.

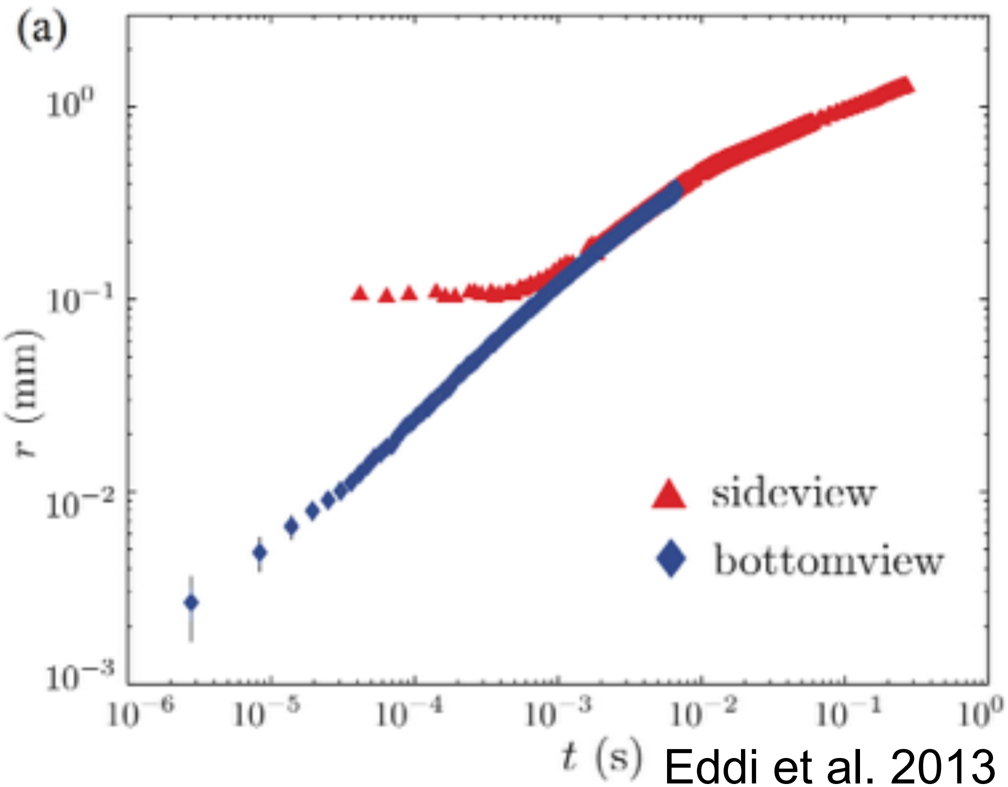
Questions about short-time spreading

- Can a spontaneous spreading process be solely described by hydrodynamic forces (e.g. inertia, surface tension, viscosity) ?

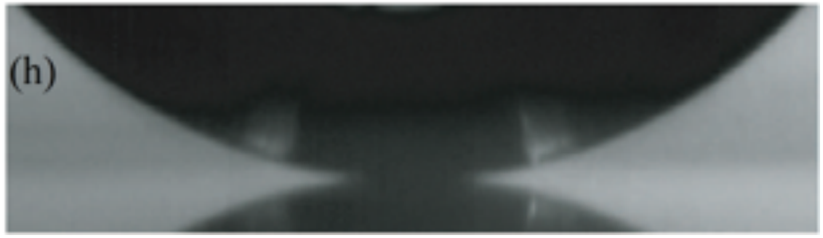
- Can micro-scale phenomena at the contact line dictate macroscopic wetting behavior ?

- Aim here is to develop a mathematical model that describes very dynamic wetting phenomena and probe the physics that govern such flow.

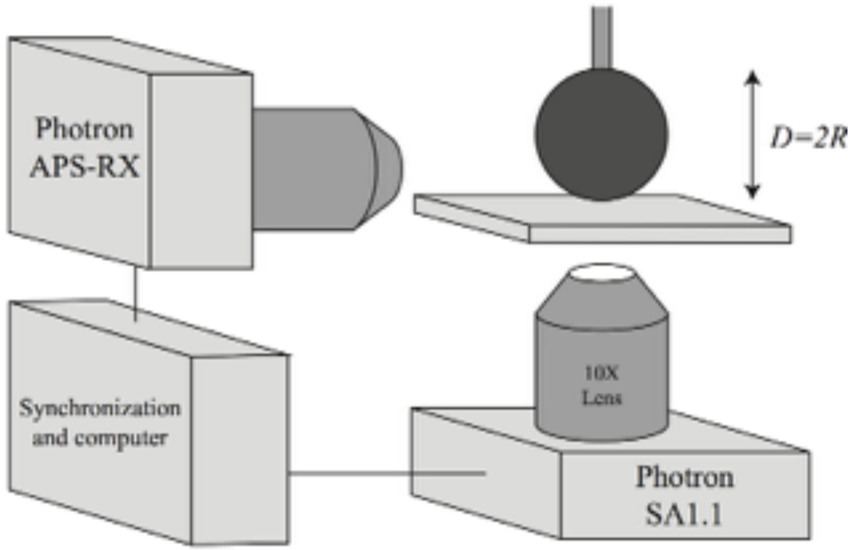
Rapid dynamic wetting, Experiments



Eddi et al. 2013

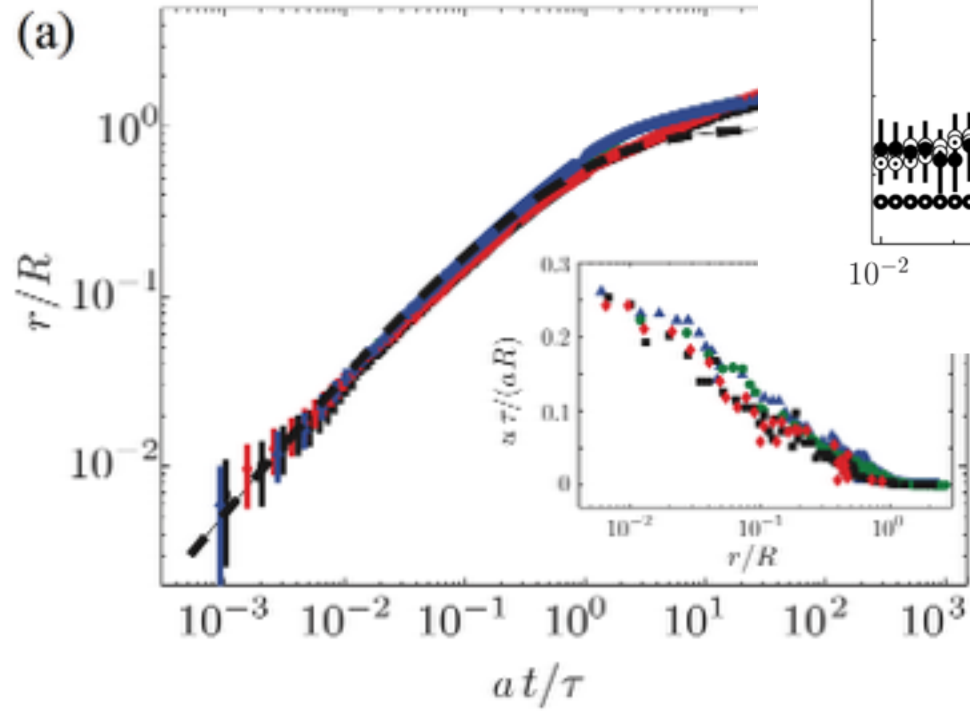


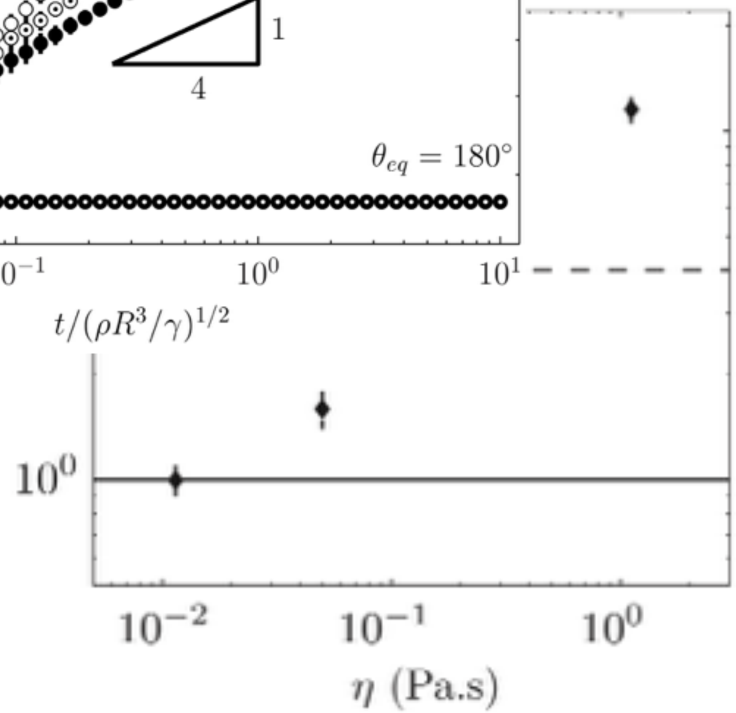
Due to the presence of a narrow gap and optical limitations, the drop image merges with its own optical reflexion on the glass substrate.

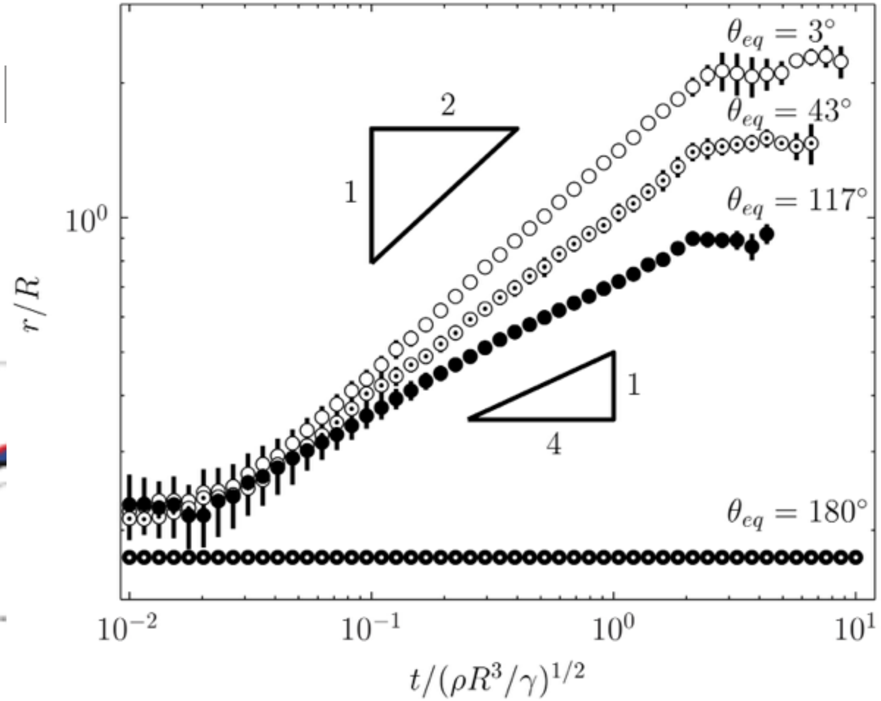


Using high-speed imaging with synchronized bottom and side views gives access to 6 decades of time resolution.

Experiment resul







While the data for different viscosities can be collapsed onto the form predicted for coalescence Fig. (a), $\tau = 4\pi\eta R/\gamma$, the typical spreading velocity does not simply scale as ~$1/\eta$. This can be seen from the prefactor a, which still displays a dependence on viscosity η, Fig. (b).

Governing equations

A binary immiscible incompressible mixture

- Navier Stokes equations:

$$\rho(C)\frac{D\mathbf{u}}{Dt} = -\nabla P + \nabla\cdot(\mu(C)(\nabla\mathbf{u} + \nabla\mathbf{u}^T)) + \phi\nabla C - \rho g \mathbf{e_z}$$

$$\nabla\cdot\mathbf{u} = 0$$

{Density (ρ), viscosity (μ), mobility (M), gravity (g)}

- Cahn-Hilliard equation:

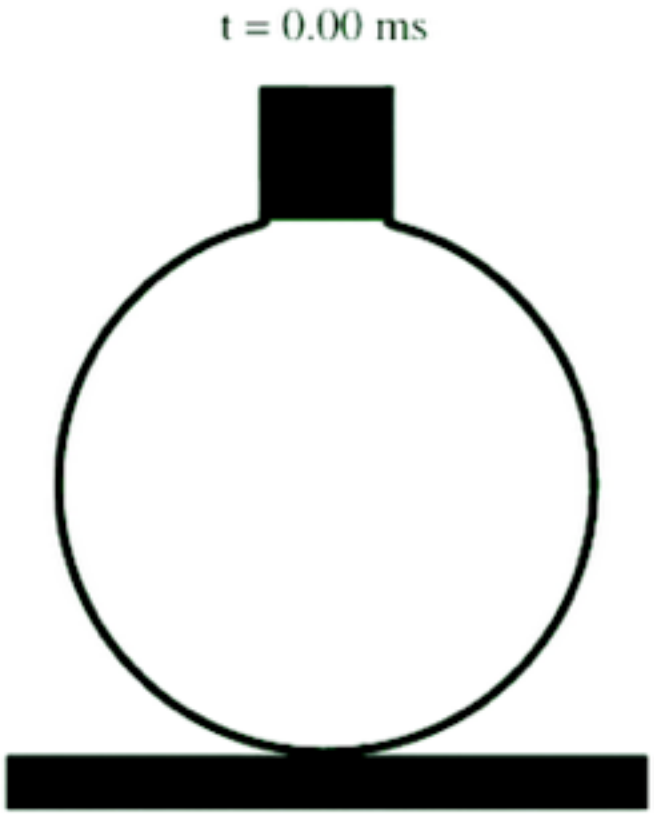
$$\frac{DC}{Dt} = M\nabla^2\phi = M\nabla^2\left(\beta\Psi'(C) - \alpha\nabla^2 C\right)$$

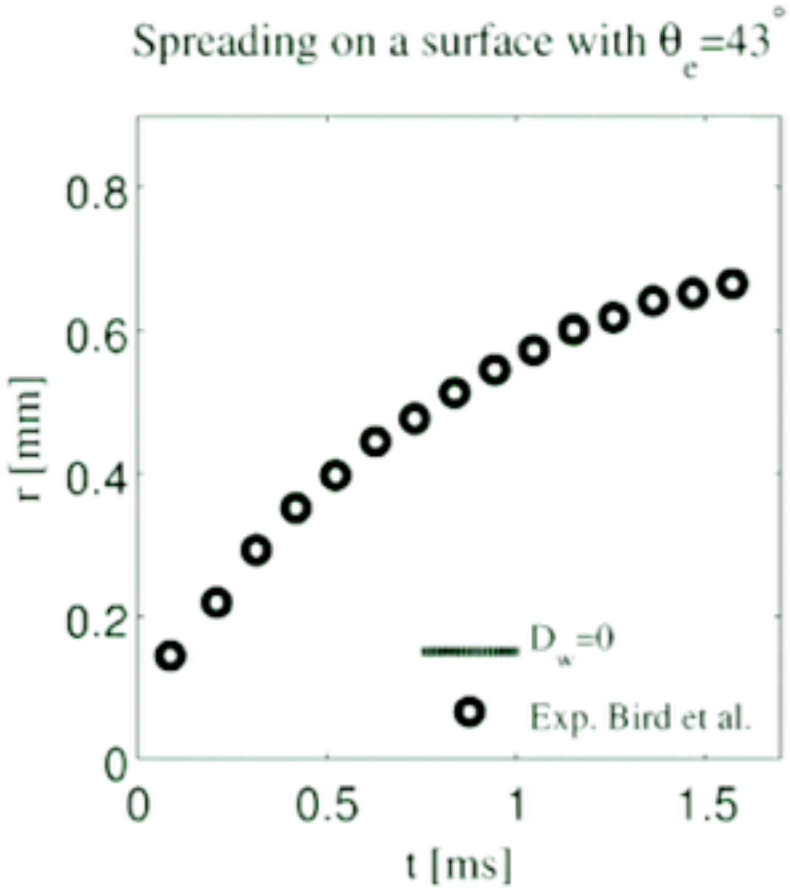
- General wetting boundary condition:

$$-\mu_f\epsilon\frac{\partial C}{\partial t} = \alpha\nabla C\cdot\mathbf{n} - \sigma\cos(\theta_e)w'(C)$$

{Friction coeff. (μ_f)}

Assuming local equilibrium





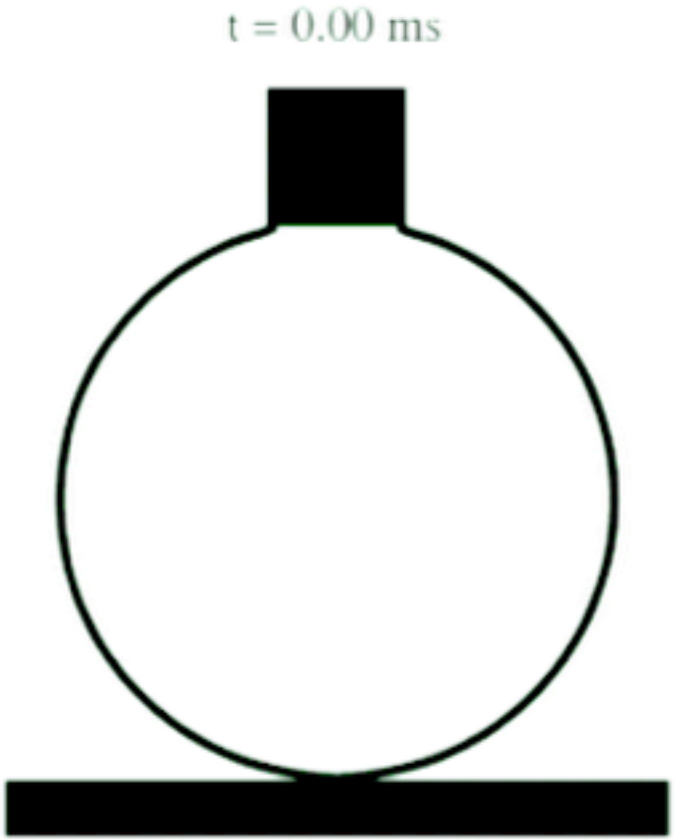
$$(\mu_f = 0)$$

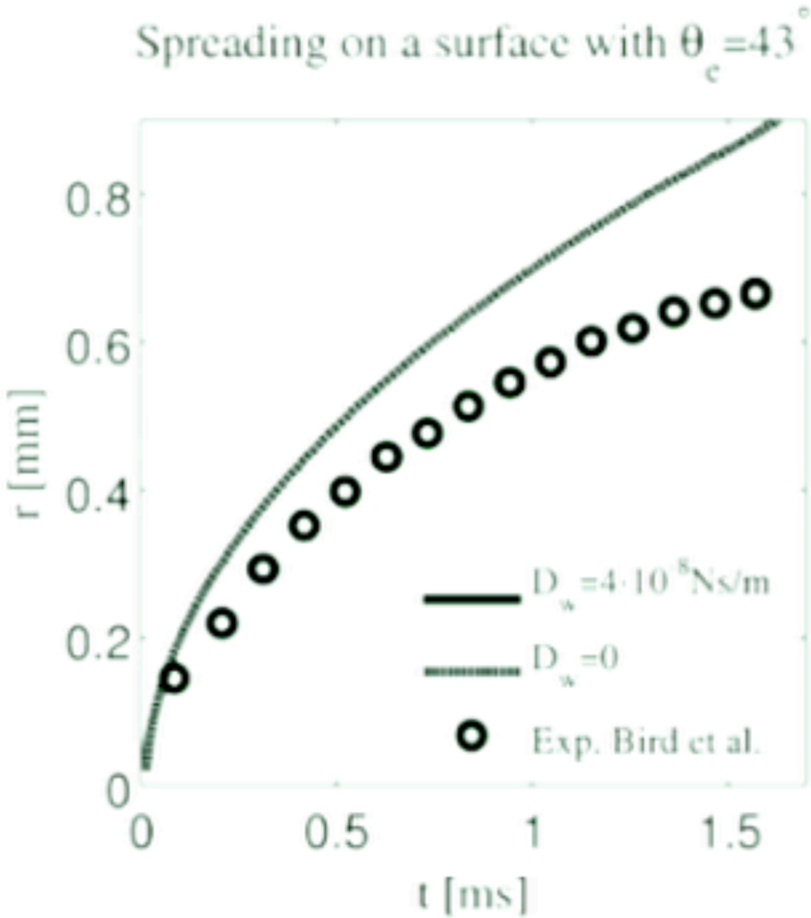
<u>Wetting boundary condition:</u>

$$0 = \alpha \nabla C \cdot \mathbf{n} - \sigma \cos(\theta_e) w'(C)$$

(Model has no adjustable parameters!)

Accounting for non-equilibrium





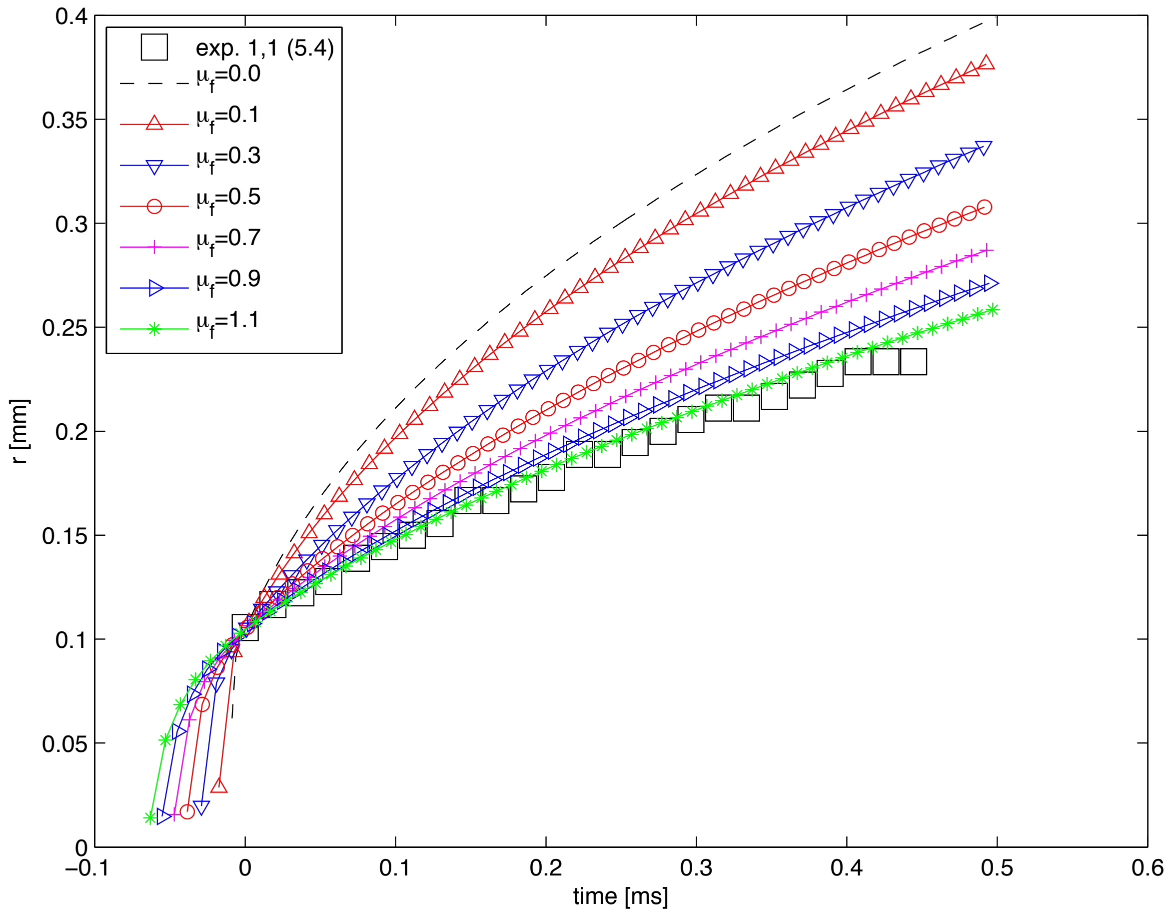
Wetting boundary condition:

$$(\mu_f = 0.07)$$

$$-\mu_f \epsilon \frac{\partial C}{\partial t} = \alpha \nabla C \cdot \mathbf{n} - \sigma \cos(\theta_e) w'(C)$$

Influence of μ_f on spreading rate

- Influence of the rate coefficient in the non-equilibrium boundary condition on spreading rate.

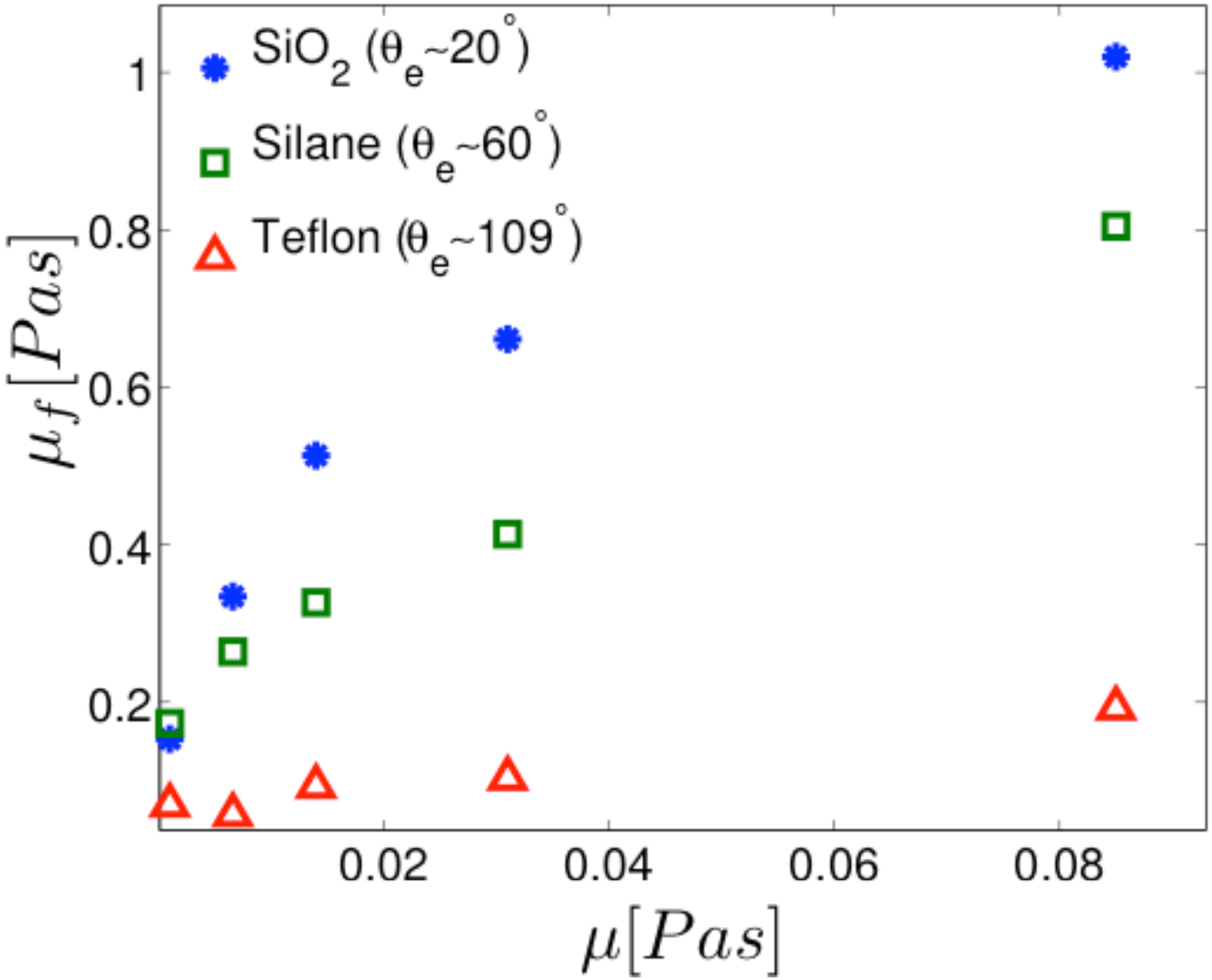


Observation from simulations

- Phase Field simulations (μ_f=0) follow hydrodynamic theory for viscously dominated wetting, results fairly independent of ε.
- For spontaneous spreading, a dissipative contribution needs to be included by having a non-zero μ_f.
- Can μ_f here represent a physically reasonable friction factor at the contact line?

Contact line friction parameter

- Measuring the contact line friction parameter for the different liquids and solid surfaces



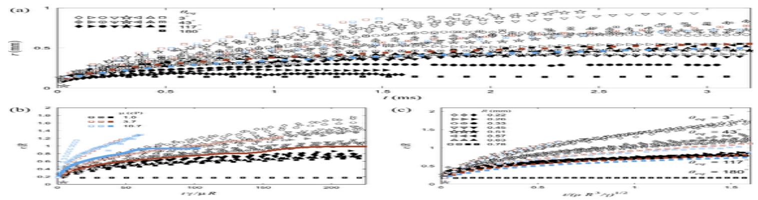
Dissipation contributions

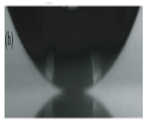
- Rate of change of kinetic energy ($\dot{R}_\rho$) :

$$\dot{R}_\rho = \int \frac{1}{2}\left(\frac{\partial \rho(C) u^2}{\partial t}\right) d\Omega$$

- Dissipation contributions; viscous dissipation ($\dot{R}_\mu$), diffusion ($\dot{R}_c$) and a contact line dissipation ($\dot{R}_f$).

$$\dot{R}_\mu = \int \frac{\mu}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T) : (\nabla \mathbf{u} + \nabla \mathbf{u}^T) d\Omega$$





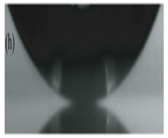
$$= \int \mu_f \epsilon \left(\frac{\partial C}{\partial t}\right)^2 d\Gamma$$

Contact line dissipation

- De Gennes[1] postulated that a dissipation would arise from the contact line region and would take the form;

$$\dot{R}_{DG} \sim \int \mu_f u_{cl}^2 dr$$

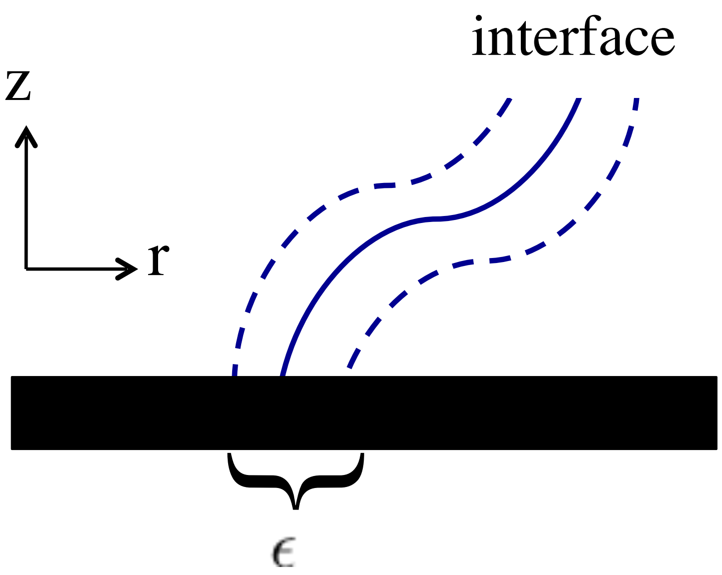
- Form of the contact line dissipation from Phase Field theory

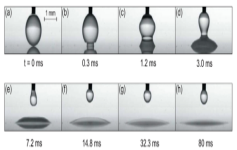
 $$= \int \mu_f \epsilon \left(\frac{\partial C}{\partial t}\right)^2 d\Gamma$$

[1] *P. de Gennes, Wetting: statics and dynamics, Rev. Mod. Phys., 1985.*

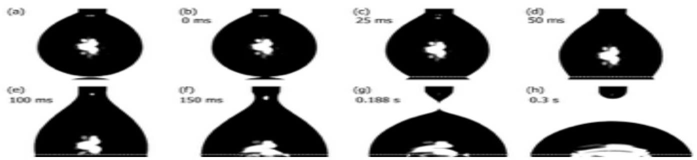
Cahn-Hilliard contact line dissipation

- Dissipation from Cahn-Hilliard model is given by:





$$= \int \mu_f \epsilon \left(\frac{\partial C}{\partial t}\right)^2 d\Gamma$$



$$\sim \int \mu_f u_{cl}^2 dr$$

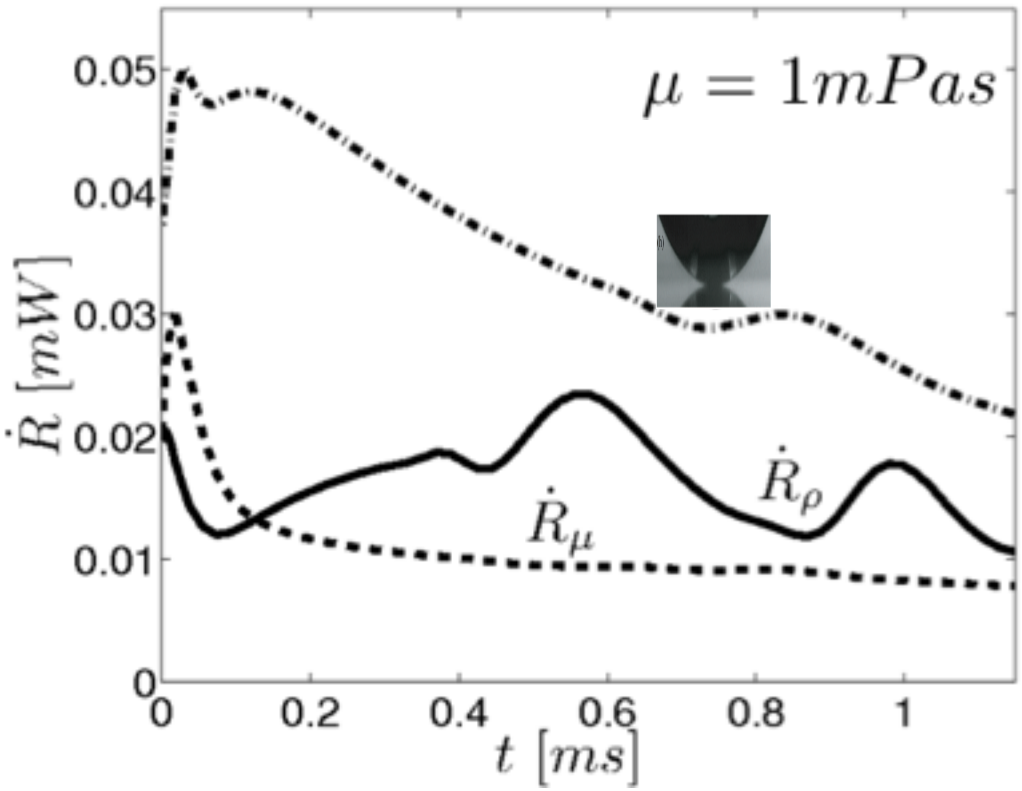
Similar form for the contact line dissipation as postulated by de Gennes!

Dissipation in dynamic wetting

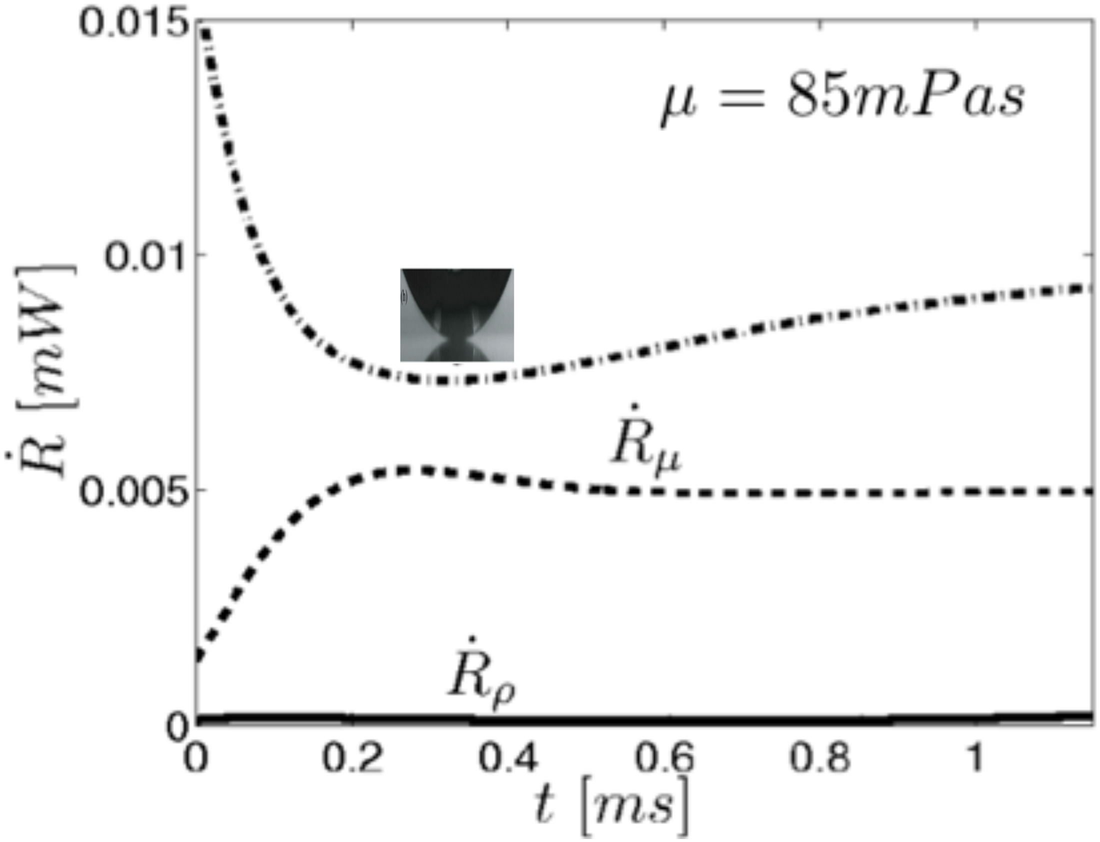
- Contact line friction dominates in dynamic wetting.

Spreading on a oxidized-Si wafer, θ_e=20°.

Water



Glycerin$_{82.5\%}$

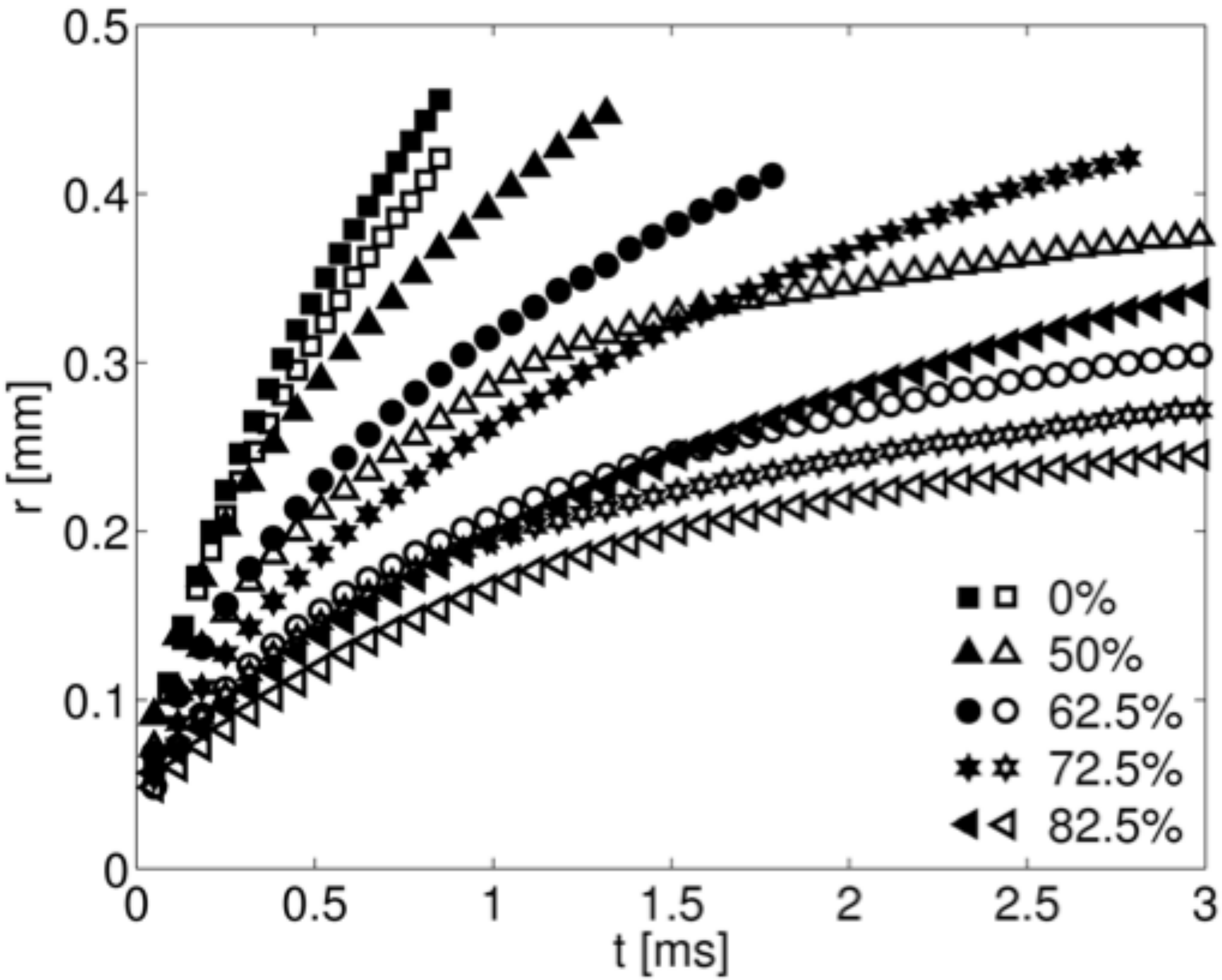


Summary of findings about dissipation in wetting

- Contact line dissipation found to govern dissipation even for very viscous liquids.
- Contact line dissipation also a larger contribution than the rate of change of kinetic energy for water.
- μ_f measured for different viscosities and surface wettability.
- Can the experiment give us further proof of the dominance of contact line friction in dynamic wetting?

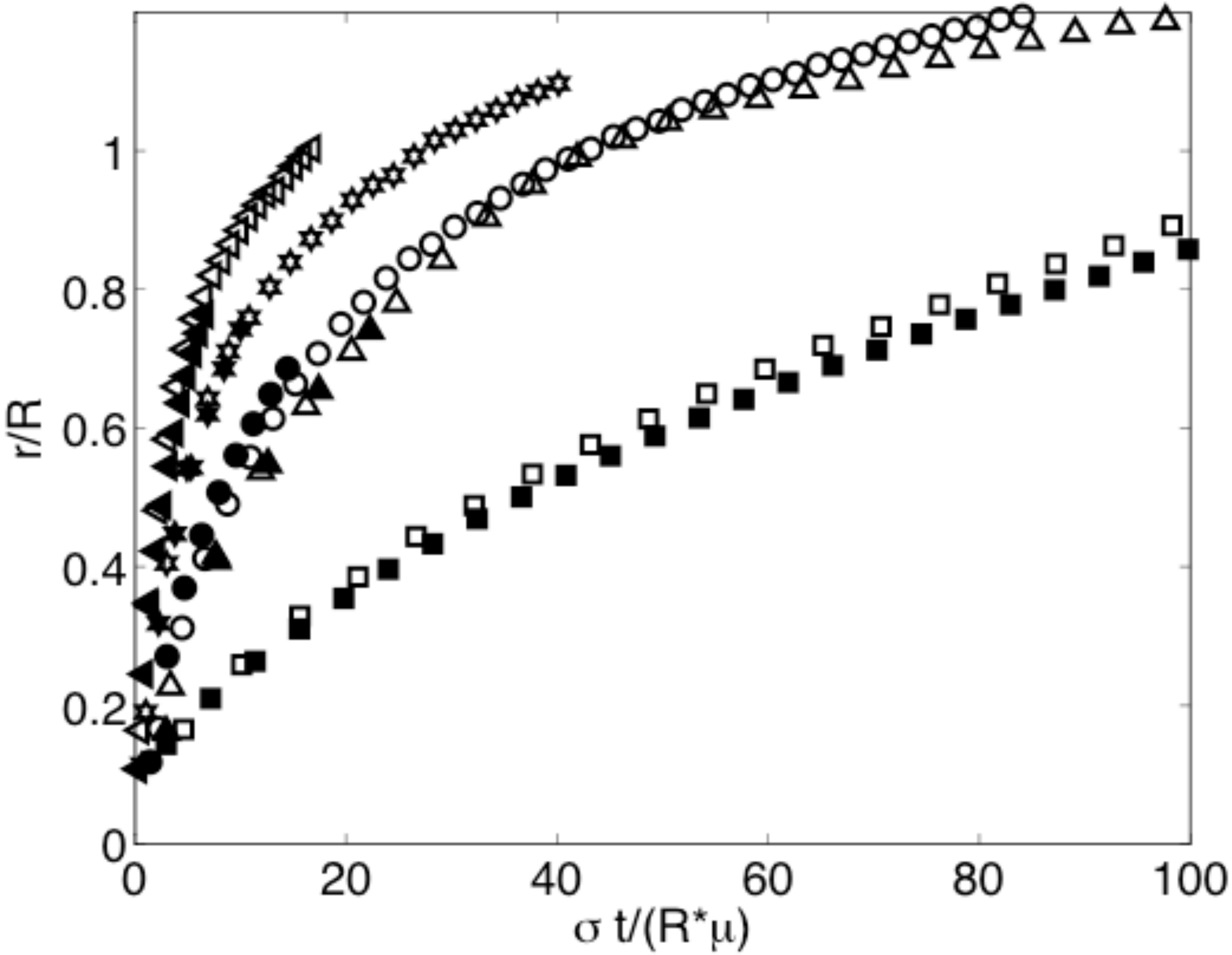
Evolution of spreading radius

- Dimensional spreading radius for different viscosities and droplet size on an oxidized Si-wafer.



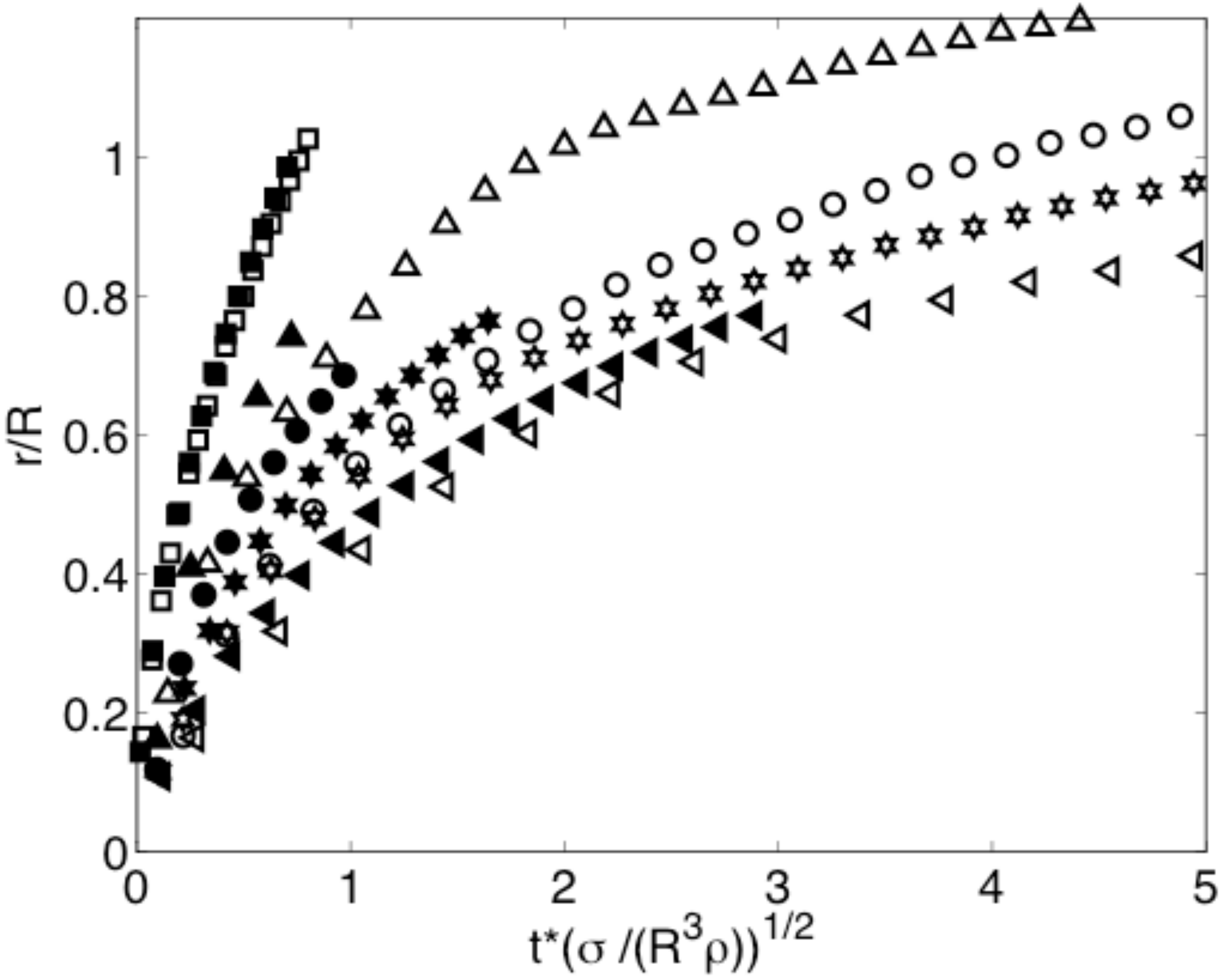
Viscous scaling

- Time-scale set by viscosity ($t^*=\sigma/R\mu$) does not collapse the data!



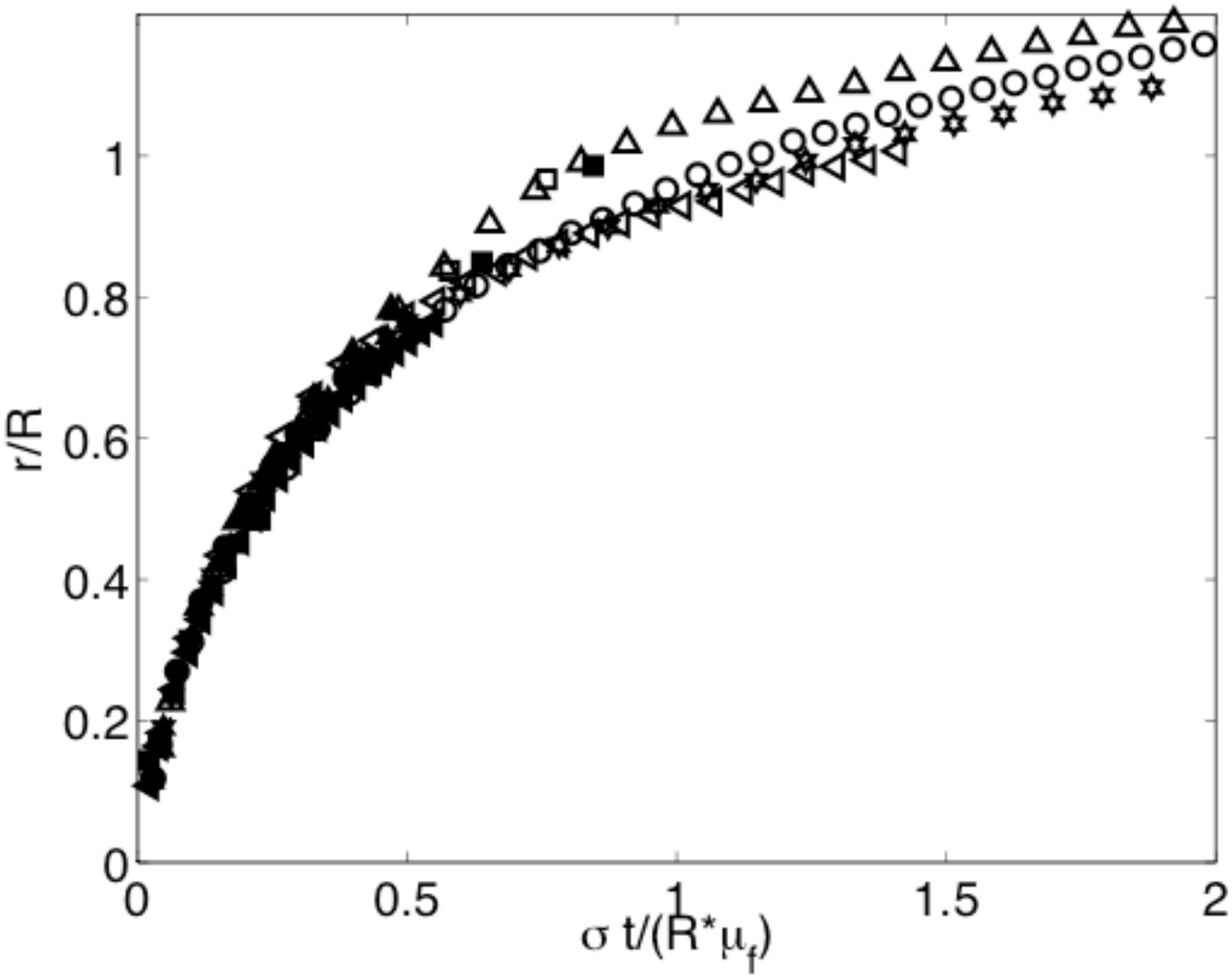
Inertial scaling

- Time-scale set by inertia ($t^{*}=\sigma/R^{3}\rho$) does not collapse the data.

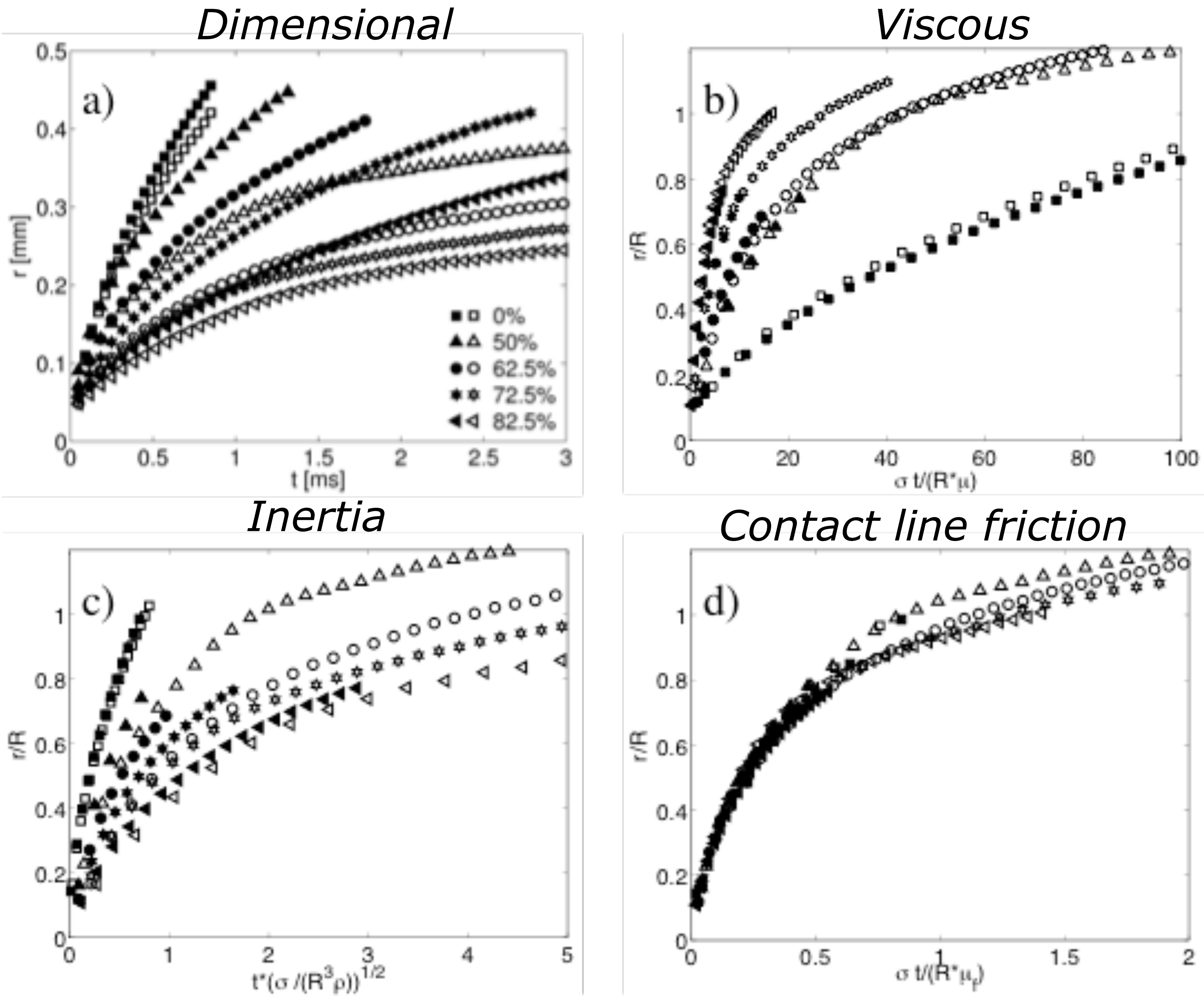


Contact line friction scaling

- Time-scale set by contact line friction ($t^*=\sigma/R\mu_f$) parameter collapses the experimental data onto a single curve!



Collapse for contact line friction scaling



Conclusions

- Contact line dissipation is found to generate a significant contribution to the total dissipation in spontaneous spreading.
- Quantitative measurement on the macro-scale of the contact line friction parameter μ_f .
- μ_f is believed to parameterize, on the macroscale, the microscopic dissipative mechanisms at the contact line.