Digital/on-demand printing

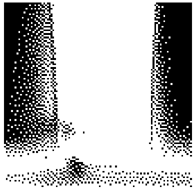
(Prof. J. Brugger)

- Basics of (inkjet) droplets
- Advanced concepts for resolution improvement (EHD, …)
- Other additive methods of relevance (LIFT, MEW,…)

CIJ & DoD Inkjet Printing

Objectives

- Understand continuous & drop-on-demand inkjet printing
- Learn how to create single drops and how they interact with the substrate



Content

- History of inkjet printing
- Methods of producing micro drops
- Drop-substrate interaction
- Drop drying phenomena
- Application examples

Material to read

Inkjet printing books

- Microdrop Generation, Eric R. Lee, CRC Press

Inkjet printing papers:

- B. Derby, Annu. Rev. Mater. Res. 40 (2010), 395-414
- Nalian et al. Langmuir 2014, 30, 44, 13470-13477
- B.J. de Gans, Advanced materials, 2004

New review:

- Detlef Lohse, Fundamental Fluid Dynamics Challenges in Inkjet Printing, Annual Review of Fluid Mechanics 2022 54:1, 349-382

Interest for single droplets science and technology is enormous

Self-confined space for conducting chemo-physical experiments, cells, interfaces, etc.

Digital droplet technologies in life-sciences.

Brief history of printing

Woodblock printing	200
Movable type	1040
Printing press	c. 1440
Etching	c. 1515
Mezzotint	1642
Aquatint	1772
Lithography	1796
Chromolithography	1837
Rotary press	1843
Hectograph	1869
Offset printing	1875
Hot metal typesetting	1884
Mimeograph	1886
Photostat and Rectigraph	1907
Screen printing	1910
Spirit duplicator	1923
Xerography	1938
Phototypesetting	1949

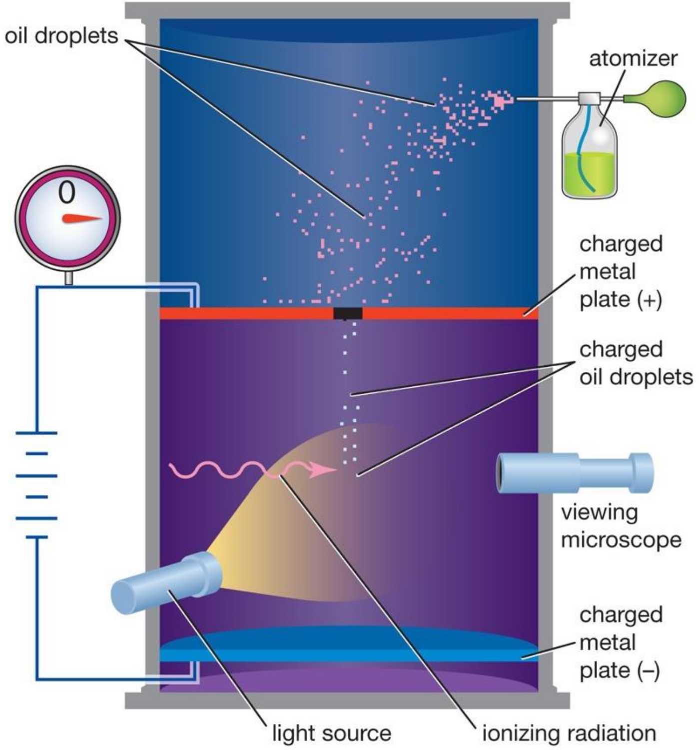
Part of a series on the

History of printing

Inkjet printing	1951
Dye-sublimation	1957
Dot matrix printing	1968
Laser printing	1969
Thermal printing	c. 1972
3D printing	1984
Digital printing	1993

V • T • E

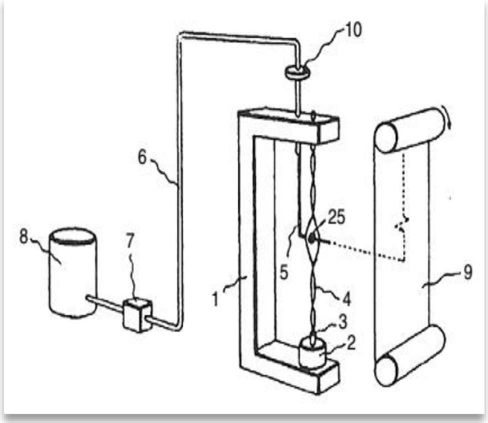
Millikan's oil drop experiment



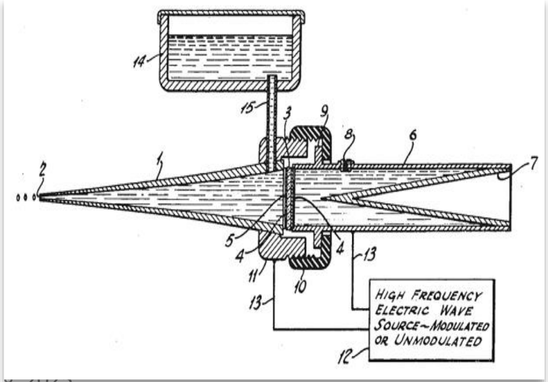
The oil drop experiment was an experiment performed by Robert A. Millikan and Harvey Fletcher in 1909 to measure the elementary electric charge (the charge of the electron). The elementary charge e is one of the fundamental physical constants and its accurate value is of great importance. In 1923, Millikan won the Nobel Prize in physics, in part because of this experiment.

Historical milestones

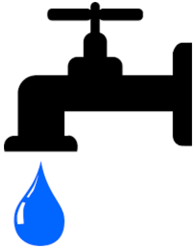
- Sweet (1965) develops continuous IJP (first device patented in 1952)
- Zoltan (1972) and Kyser & Sears (1976) develop drop-on-demand (DOD) IJP
  (first device patented in 1950)
- IJP used to produce DNA microarrays played a major role in the Human Genome Project (late 1990's)



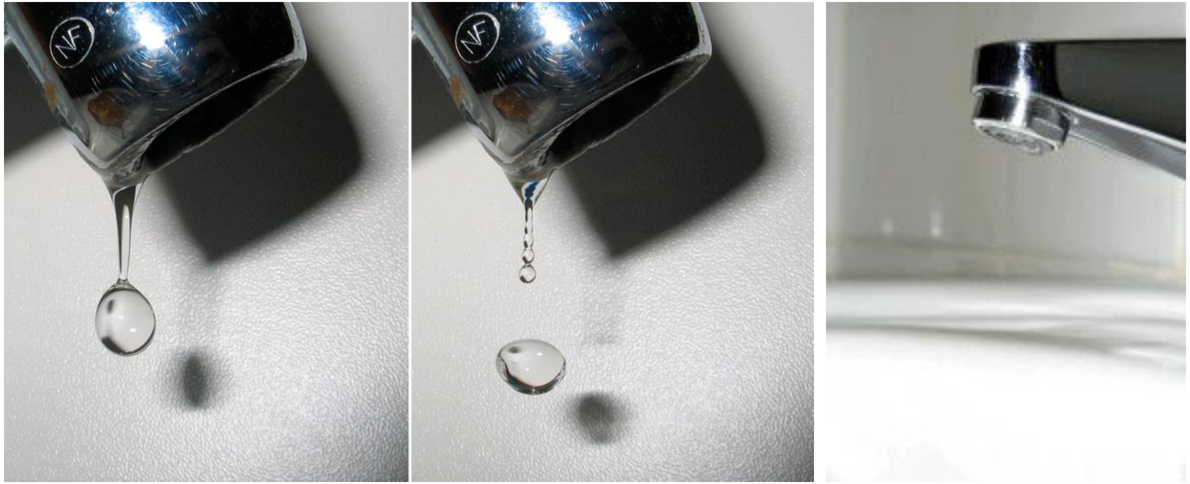
First CIJP device (1952)

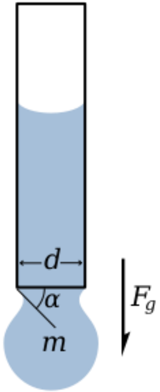


First DOD IJP device (1950)



About drops





https://commons.wikimedia.org/wiki/File:Pendant_drop_test.svg#/media/File:Pendant_drop_te
st.svg

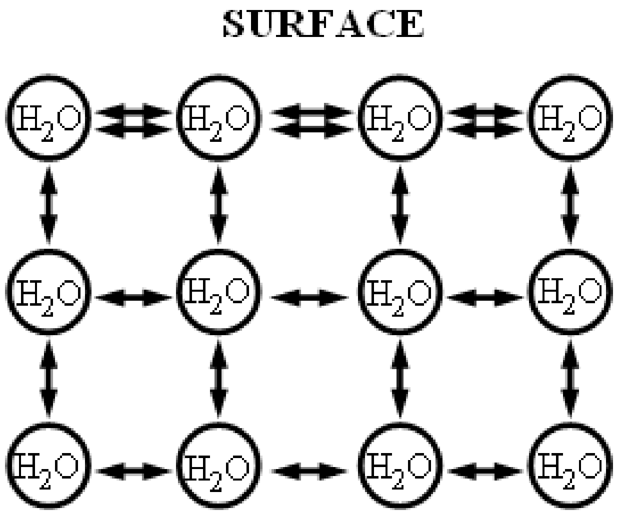
https://www.gettyimages.ch/detail/video/high-speed-extreme-close-up-
water-drops-falling-stock-videomaterial/605-18

$$F_\gamma = \pi d \gamma$$

$$mg = \pi d \gamma \sin \alpha$$

$$mg = \pi d \gamma$$

Surface tension (reminder)



Surface tension—molecules at the surface form stronger bonds

Q: Capillary length of water?

$L_{cap} = (\gamma / \rho g)^{1/2}$

A

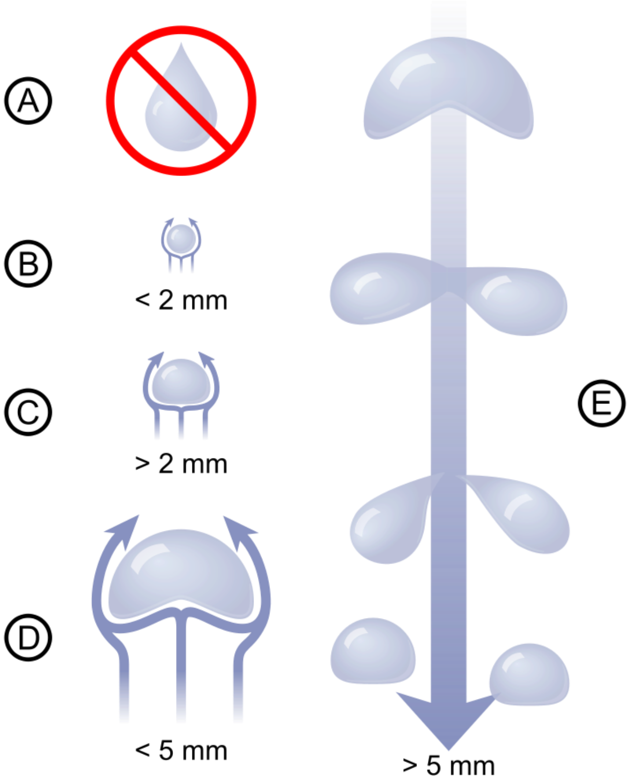
Some numbers as scale reference

Table 1.1 Size Range of Microdrop Dimensioned Objects

Object	Size in Microns
Tobacco smoke	0.25
Virus	0.1
Compacted DNA (5000 base pairs)	0.04–0.2
IC manufacturing photolithography limit	0.2
Bacteria	1
Open DNA strand (5000 base pairs)	1
Standard pigments	1–5
Inkjet pigments	0.1
Red blood cell	8
SLAC automated Millikan drops	7–20
Typical animal cell	10
Flour dust	15–20
Inkjet printer drop	18–40
Pollen	15–70
Spray can mist	1–100
Human hair diameter	100

- Microdrop Generation, Eric R. Lee, CRC Press

Drop shapes



https://commons.wikimedia.org/wiki/File:Raindrops_sizes.svg#/media/File:Raindrops_sizes.svg

$$V = \frac{4}{3}\pi r^3$$

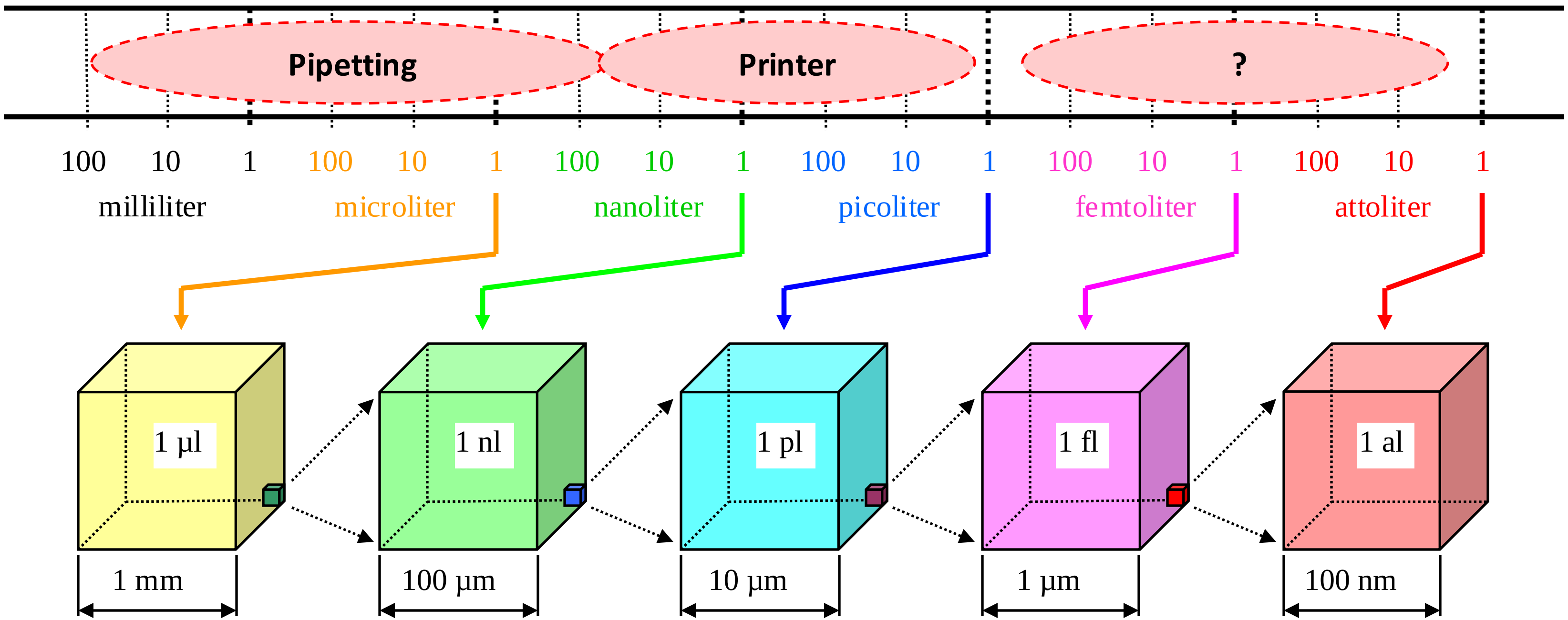
Some numbers

Table 1.2 Volume and Mass of Microdrops

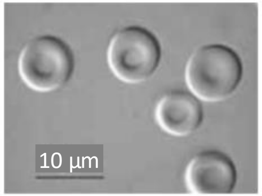
Drop Diameter (Microns)	Drop Volume (Liters)	Drop Mass (Grams)	Drop Mass (Gev)
0.1	5.2×10^{-19}	5.2×10^{-16}	2.9×10^{8}
0.5	6.5×10^{-17}	6.5×10^{-14}	3.7×10^{10}
1.0	5.2×10^{-16}	5.2×10^{-13}	2.9×10^{11}
5.0	6.5×10^{-14}	6.5×10^{-11}	3.7×10^{13}
10.0	5.2×10^{-13}	5.2×10^{-10}	2.9×10^{14}
25.0	8.2×10^{-12}	8.2×10^{-9}	4.6×10^{15}
50.0	6.5×10^{-11}	6.5×10^{-8}	3.7×10^{16}
100.0	5.2×10^{-10}	5.2×10^{-7}	2.9×10^{17}

- Microdrop Generation, Eric R. Lee, CRC Press

Small volume dispensing

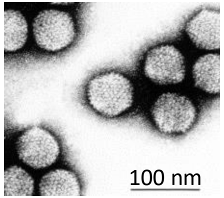


Human red cell



physwww.physics.mcmaster.ca

Adenovirus



www.ncbi.nlm.nih.gov

Methods of producing mono-disperse micro drops in free-flight*

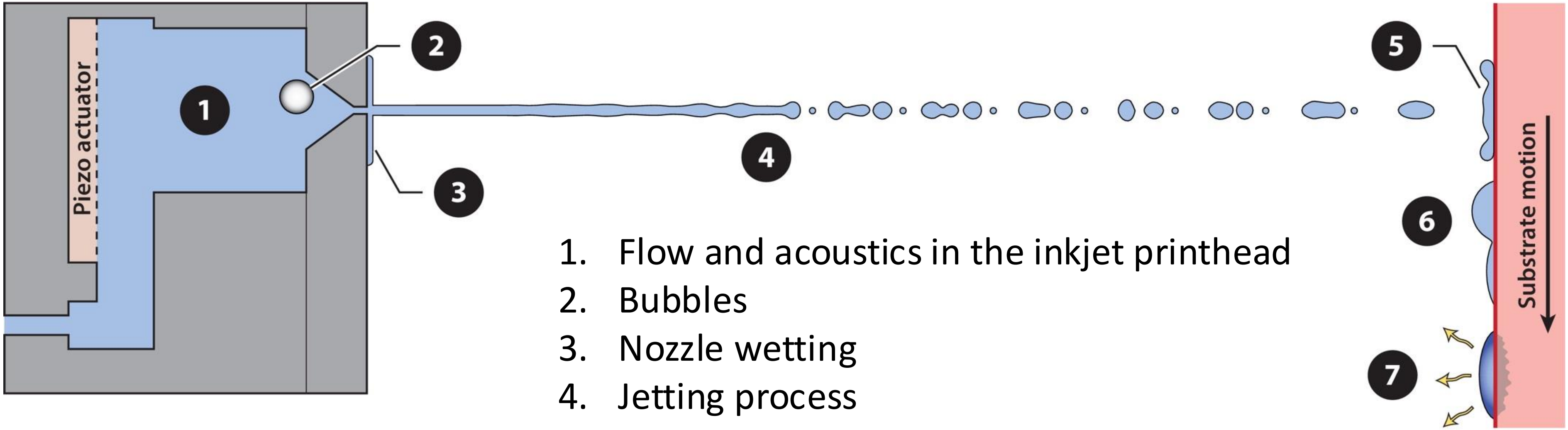
*not by contact

CJP versus DOD

Water jet becomes unstable

Oil is different
Hot chocolate fountain

7 events and physical processes



1. Flow and acoustics in the inkjet printhead
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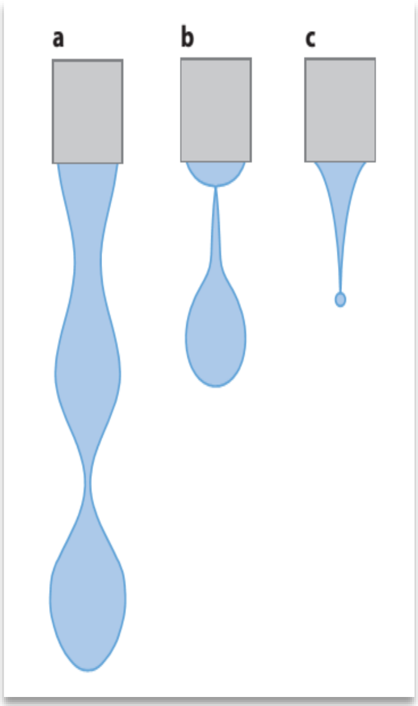
7. Drop evaporation and solidification

Lohse D. 2022
Annu. Rev. Fluid Mech. 54:349–82

Forming microdroplets from a nozzle



Continuous DOD Tip streaming (field- or flow-induced)

Basaran *et al.*, *Annu. Rev. Fluid Mech.* 2013

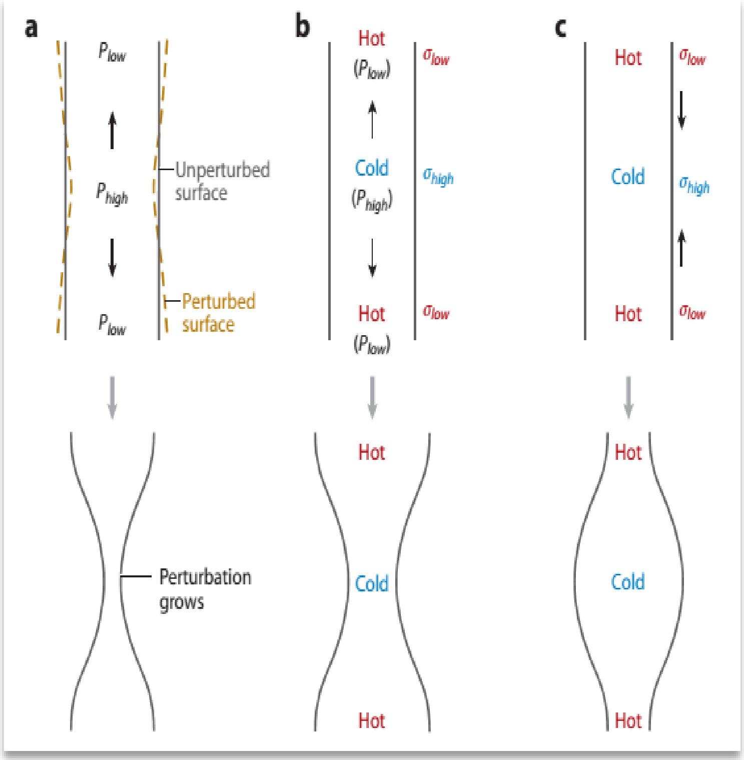
Drop generation by continous jet

Drop generation typically results from the instability of a liquid column through an external perturbation

a. Rayleigh-Plateau (capillary) instability:
mechanical perturbation

b. Thermal-capillary:
pressure gradient

c. Marangoni (thermocapillary):
surface tension gradient

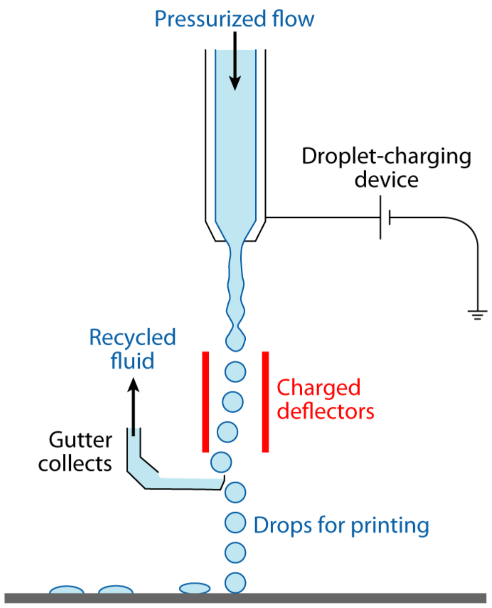


Basaran *et al.*, *Annu. Rev. Fluid Mech.* 2013

Continuous inkjet printing

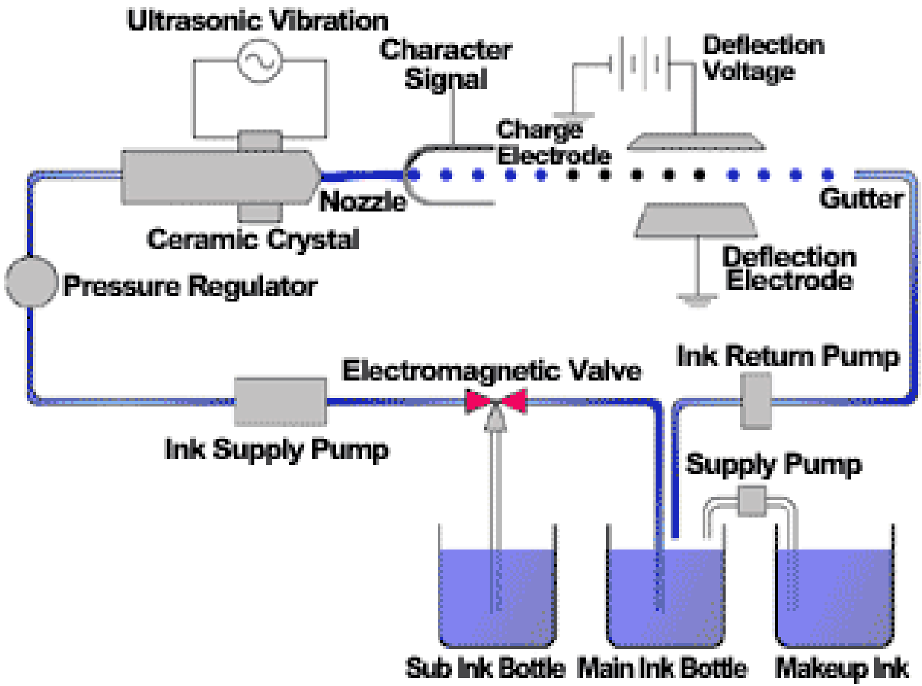
- General principle
  - A jet is pushed out of the nozzle by pressure
  - The liquid column is broken into drops by the Rayleigh instability

- Additional features
  - Drops are charged by nozzle potential relative to ground
  - Deflector plates: drops either toward substrate or toward gutter and recycled (unwanted drops)



Derby B. 2010.
Annu. Rev. Mater. Res. 40:395–414

Continuous inkjet printing

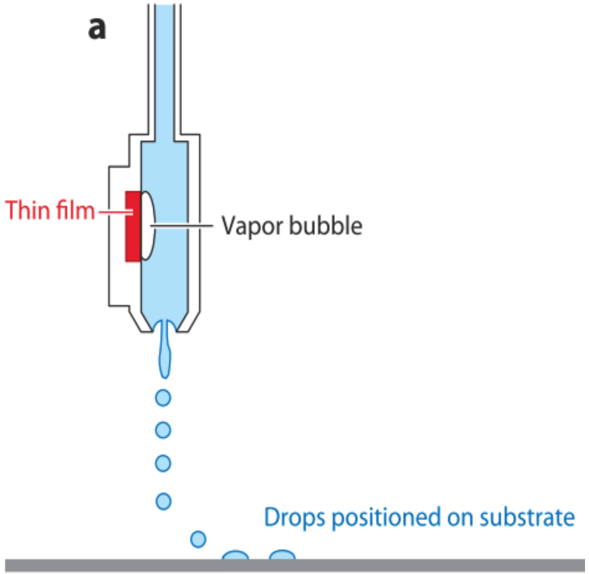


From CJP versus DOD:

we need to induce a perturbation/momentum as f(t) to a liquid volume so that it overcomes the surface tension and can form droplets

DOD IJP - Thermal IJP

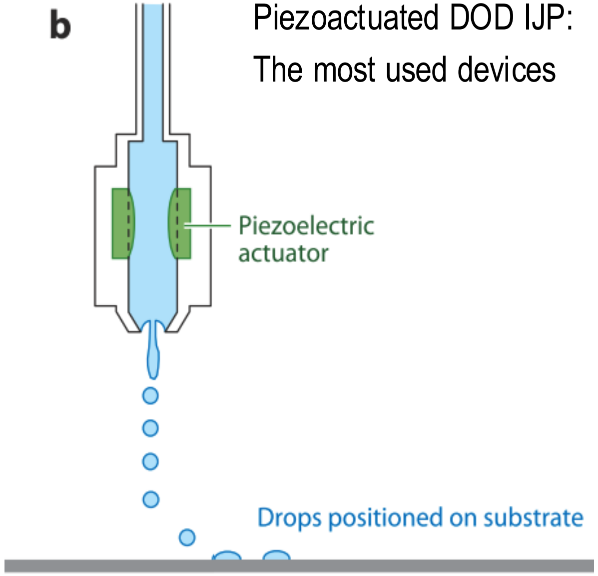
- Thermal IJP (a.k.a. “Bubble jets”)
- A metallic element (e.g. thin film resistor) is heated generating a bubble which collapses shortly afterwards
- The collapse leads to a pressure wave which propagates until the tip of the nozzle
- At nozzle tip the pressure wave generates a drop (on demand)
- Easy to integrate into dense arrays of nozzles
- High speed printing
- Affordable
- Dominate the low-end color printer market



B. Derby, Annu. Rev. Mater. Res. 2010

DOD IJP - Piezoactuated IJP

- A piezo-element (i.e. piezoelectic actuator) receives an electric pulse and induces a compression (small deformation) of the capillary tube.
- This leads to the formation of a pressure wave which propagates through the capillary in both directions.
- At the nozzle tip, the sum pressure wave will break the jet of liquid, generating a drop

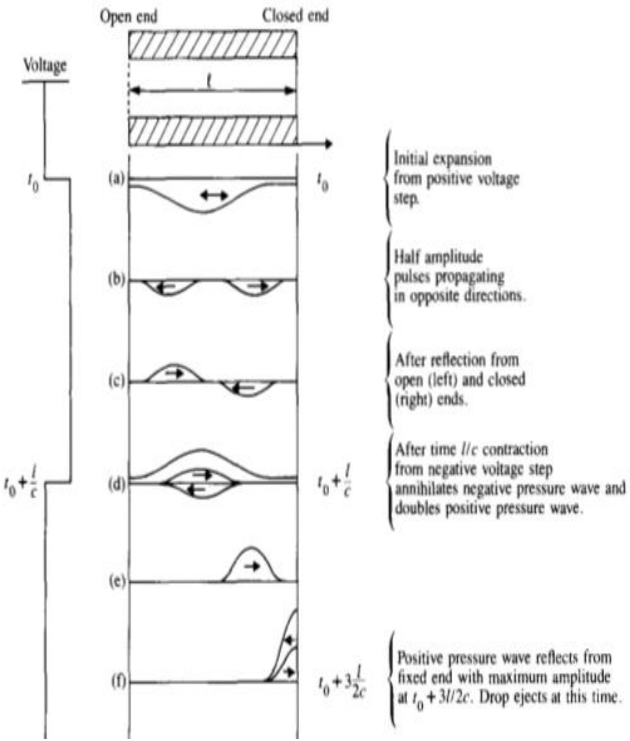


Piezoactuated DOD IJP:
The most used devices

B. Derby, Annu. Rev. Mater. Res. 2010

DOD IJP - Piezoactuated IJP

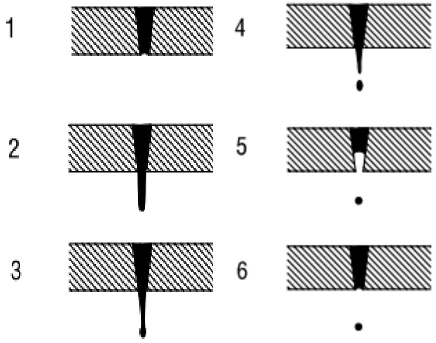
1. Capillary compression (pressure)
2. Wave propagates in both directions
3. Reflections on both ends
4. The waves meet again when new impulse is applied
5. One wave (toward open end) is annihilated while other one is enhanced
6. The pressure is 4x the applied one
   → Drop generation



D. B. Bogy and F. E. Talk " Experimental and Theoretical Study of Wave Propagation Phenomena in Drop-on-Demand Ink Jet Devices". IBM J. RES. DEVELOP., 28 (3), 1984

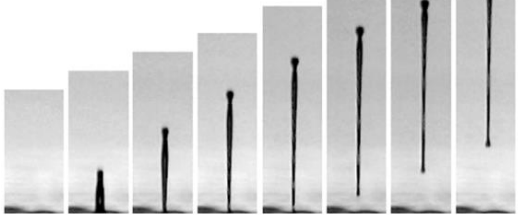
DOD IJP - Piezoactuated IJP

1. Equilibrium
2. Ejection and Fluid jet generation
3. Fluid jet destabilization
4. Drop break off (at the position of the largest jet curvature variation) and fluid jet withdraw
5. Capillary action refill
6. Ready to eject



E. Lee, *"Microdrop Generation"*, CRC Press 2003

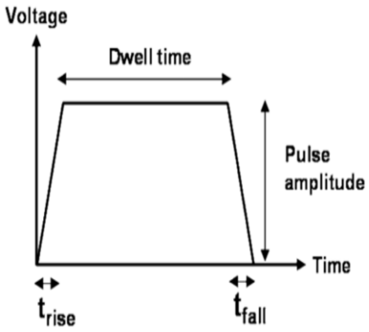
Experimental



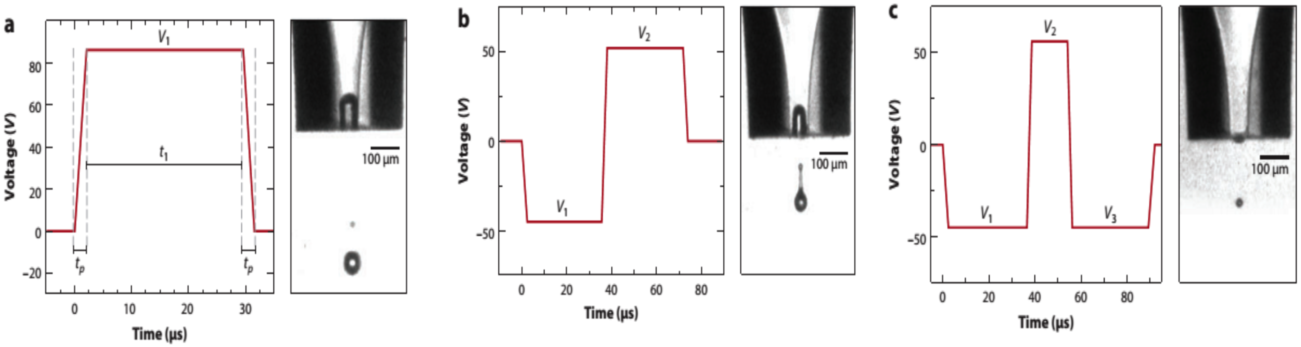
H. Wijshoff , *Phys. Rep.* 491 (2010)

Drop size modulation by pulse shaping

- Typical pulse parameters
  - Pulse amplitude
  - Rise, Dwell and Fall times
- Varying pulse parameters enables to create droplets with smaller diameter than the nozzle orifice



Basaran *et al.*, *Annu. Rev. Fluid Mech.* 2013



Thermal vs Piezo IJP

Thermal IJP

- Drop-on-demand system
- Thermal actuation (bubble)
- Heat generation
- Cannot be used with thermal sensitive inks
- Lower resolution
- Lower durability (heating damages the heads over time)
- Lower costs of production

Piezo IJP

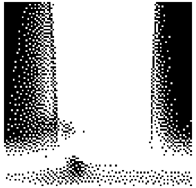
- Drop-on-demand system
- Piezo actuation
- No heat generation
- Do not damage the ink
- Larger range of ink compatibility
- Better durability
- Higher resolution
- Higher costs of production

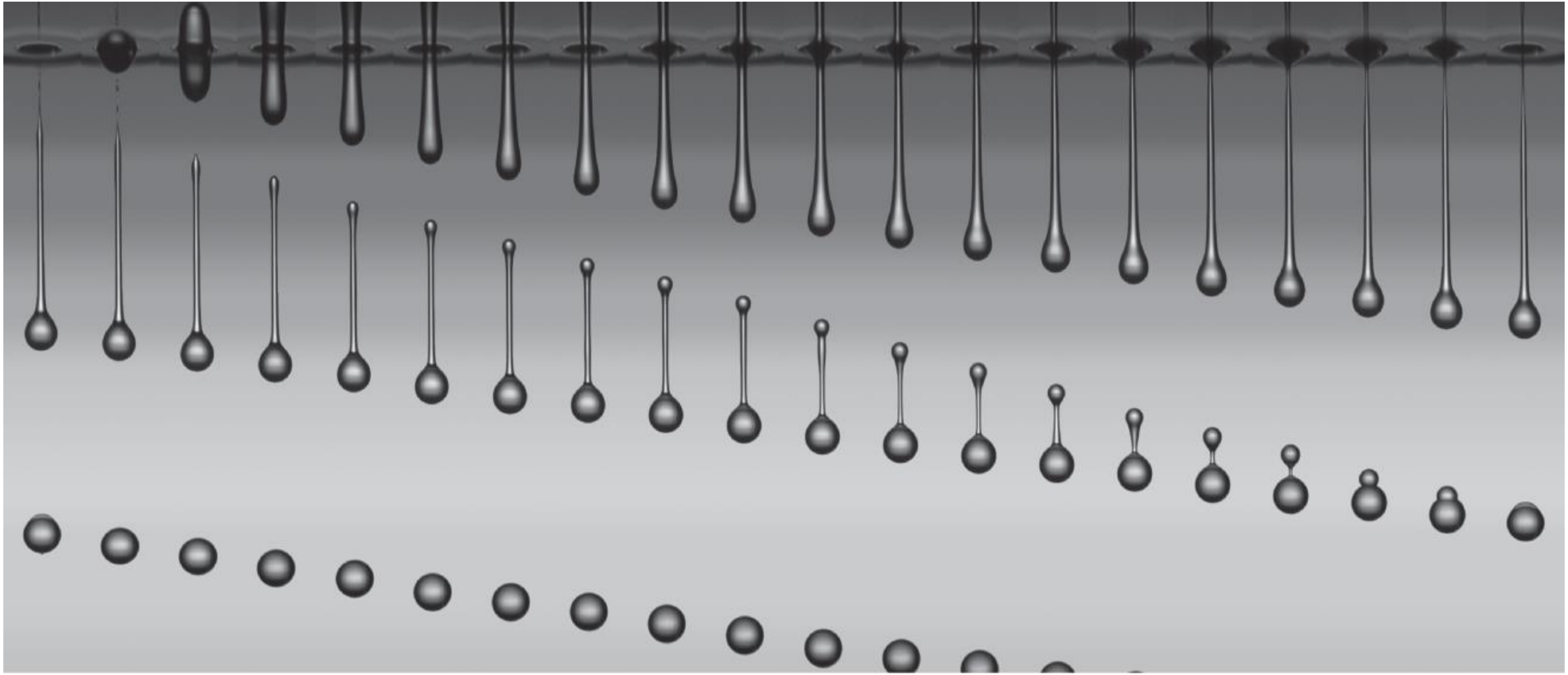
How to observe inkjet drops?

High speed camera:

[drop ejection video]

Stroboscope





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How to design inks that can be printed?

Relevant dimensionless numbers

General parameters that determine inkjet printability

- **Ink**: Density (ρ), Surface tension (σ), Dynamic viscosity (μ)
- **System**: Liquid velocity (v), Characteristic length (L), Nozzle aperture diameter (d)

Relevant dimensionless numbers:

- Reynolds number, Re (~inertia/viscosity)
- Weber number, We (~inertia/surface tension)
- Ohnesorge number, Oh
- Parameter Z (defined by Fromm, 1984):

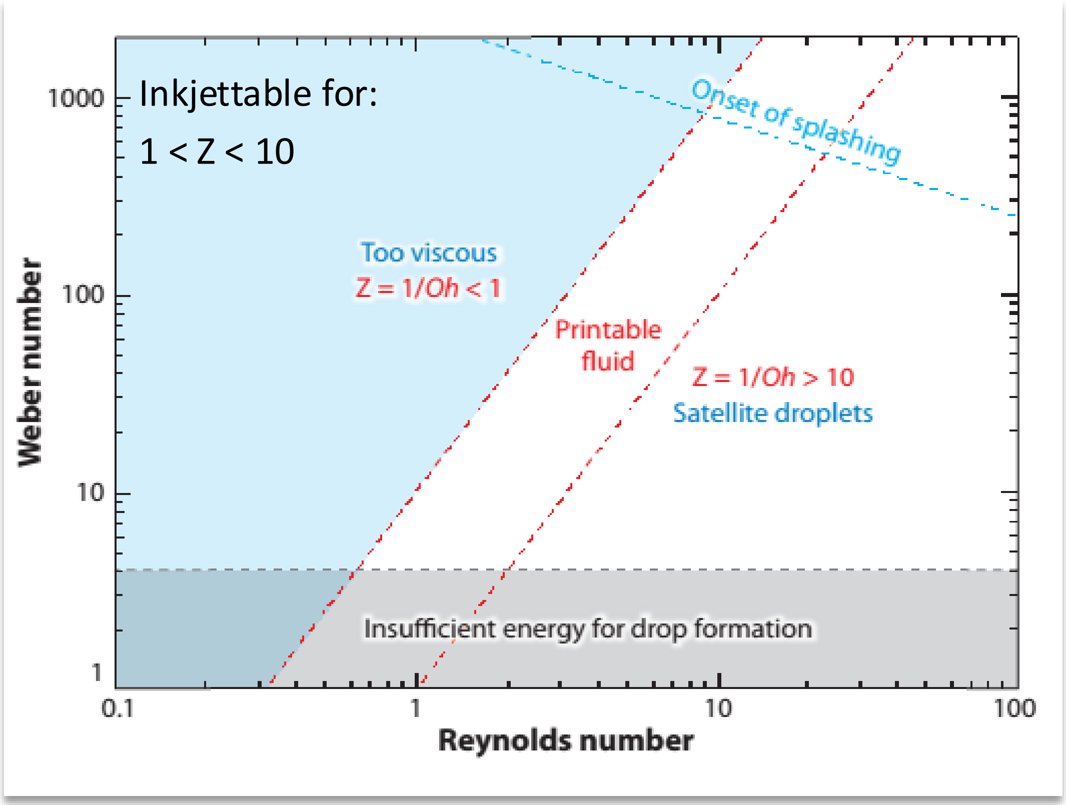
$$Re = \frac{\rho v L}{\mu}$$

$$We = \frac{\rho v^2 L}{\sigma}$$

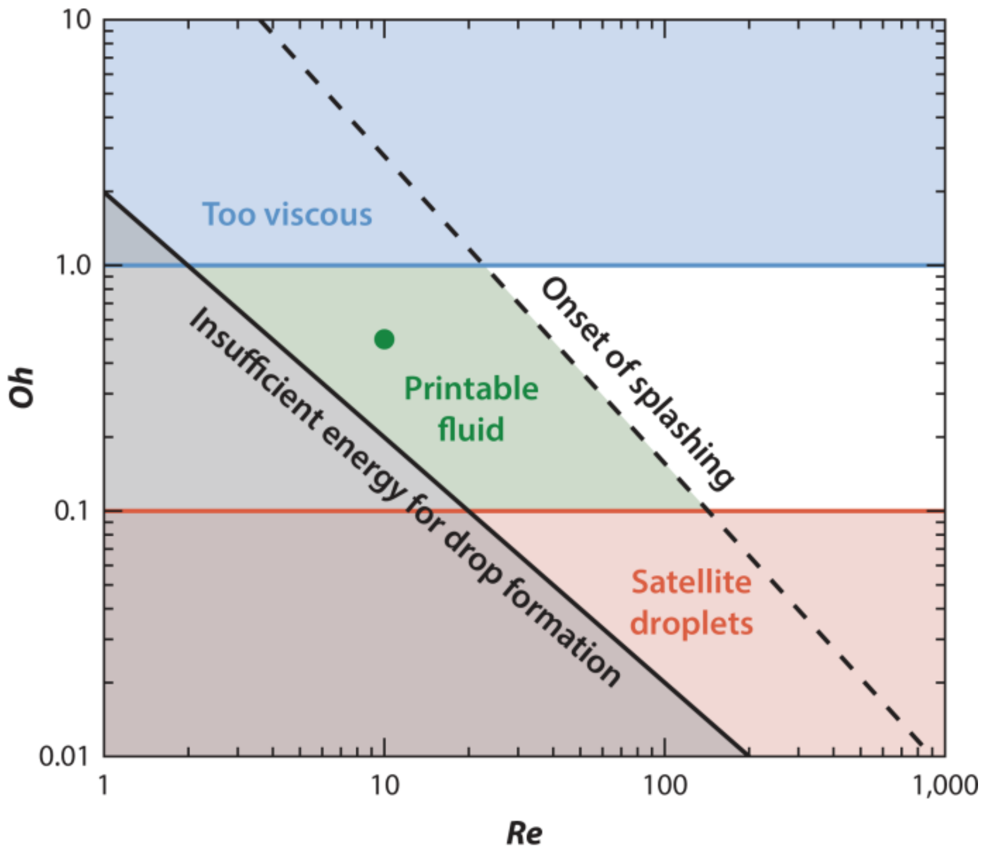
$$Oh = \frac{\mu}{\sqrt{\rho \sigma L}} = \frac{\sqrt{We}}{Re}$$

$$\mathrm{Z} = 1/\mathrm{Oh}$$

(Polymer) Ink printability



Derby, *Annu. Rev. Mater. Res.* 2010



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Reynolds number
Weber number
Capillary number
Ohnesorge number
Deborah number
Womersley number
Stokes number
Péclet number
Schmidt number
Prandtl number
Lewis number
Marangoni number
Damköhler number

Newtonian / Non-Newtonian solutions

Newtonian fluids

- Viscous stresses arising from flow are linearly proportional to the local strain (i.e. viscosity is independent of shear rate)
- Examples : Water, Mineral oils, fluids with low molecular weight

Non-newtonian fluid (typically polymers)

- For most of non-Newtonian fluids, viscosity decreases with increasing shear rate
- General mechanism: Uncoiling and decoupling of entangled polymer chains, which under high shear can move independently and align with the direction of the fluid flow (=> Viscosity reduction for limited range of shear rates).
- Examples : Blood, Paints, fluids with long polymer chains …

Influence of polymer molecular weight

Example of polymer containing ink with different M_W

- **Newtonian** (short filament length and absence of satellites)
  a) Glycerol / Water
- **Non-Newtonian** (long filament length and presence of satellites)
  b) 0.3 % M_w of 100'000 poly(ethylene oxide)
  c) 0.1 % M_w of 300'000 poly(ethylene oxide)
  d) 0.05 % M_w of 1'000'000 poly(ethylene oxide)
  e) 0.043 % M_w of 5'000'000 poly(ethylene oxide)


(a)


(b)


(c)


(d)


(e)

B.J. de Gans, *Adv. Mater.* 2004
Y . Christianii *et al., J. Rheol. 2002*

Inkjet printing of polymers

- **Main characteristics for the case of polymers**
  - Drop generation characterized by an elongating filament (as observed precedent slide a-e)
  - The disintegration of the filament begins with the formation of a pinch point above the main droplet and satellite droplets along the filament before rupture occurs
  - Above a certain concentration, the capillary force is not able to break the filament and the ejected droplet retracts back into the nozzle.

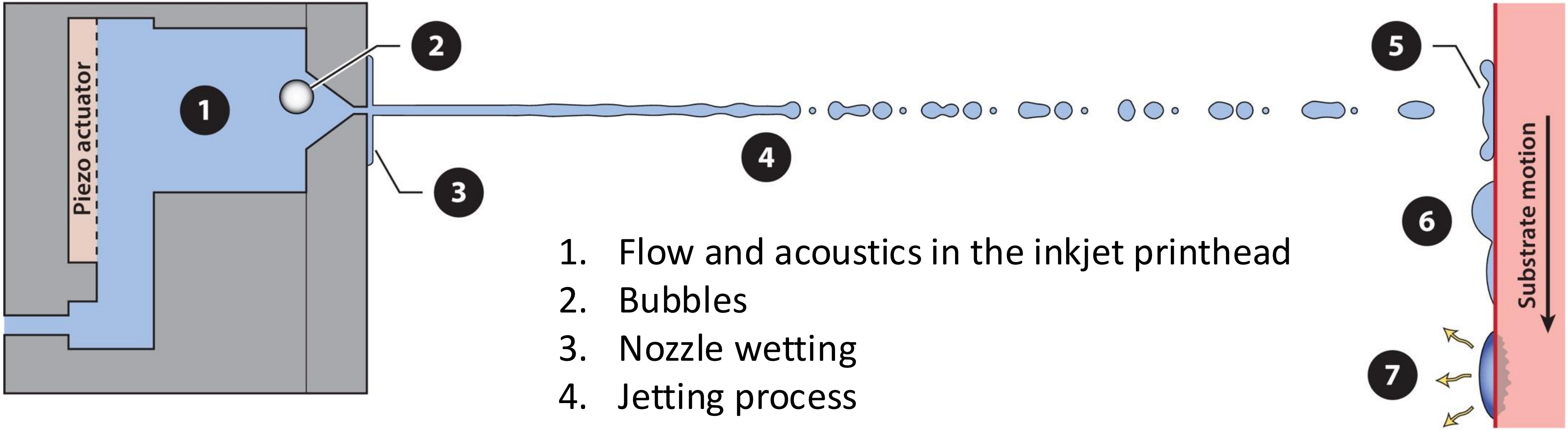
Inkjet printing of polymers

- **Summary**
  - Typically viscosities of polymeric solutions (non diluted) are in the range of 0.5 – 10 Pas
  - Polymers are usually inkjet printed as diluted solutions (with solvents)
    - Allows reducing the viscosity (similarly as for thin layers after spin-coating)
  - Solutions of polymers directly inkjet printable (solvent free) with low viscosities (approx. 20 mPa-s) are commercially available
  - The type of monomers / oligomers which are in the solution implies a more or less non-Newtonian behavior

IJP 3 Steps

1. Inkjet printing is about formation of ultra small droplets
2. Positioning the droplets precisely on the substrate
3. Drying process to form the pattern directly to any kind of substrate

7 events and physical processes



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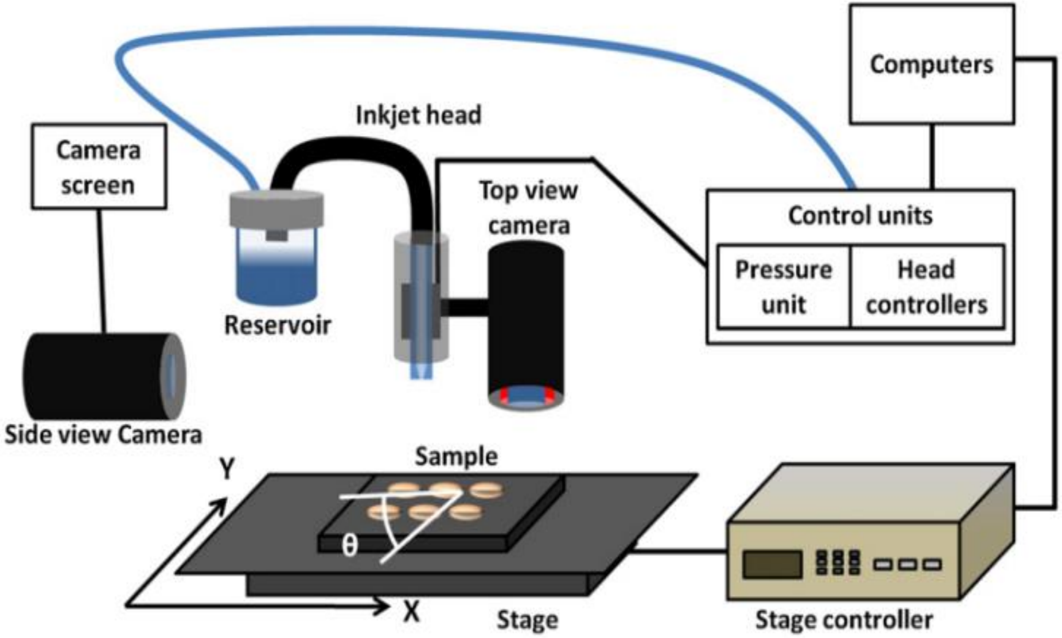
IJP: example of an experimental setup



[Jacot-Descombes *et al.*, *J. Micromech. Microeng.* 22, 2012]

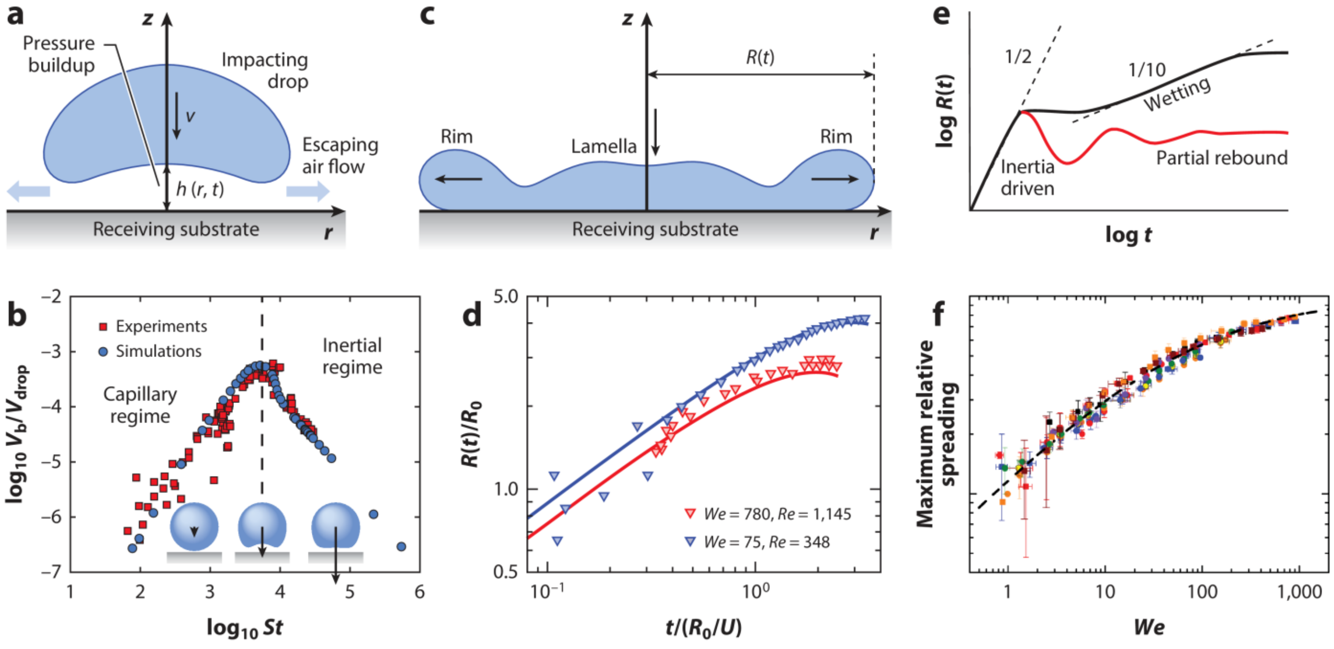
Drop/substrate interaction

video drop landing

Drop/substrate interaction

- Impact spreading - Final shape
- Drops on unpatterned substrates
- Surface Energy – Wenzel / Cassie-Braxter states
- Drops on patterned substrate
- Liquid confinement on substrates

Droplet impact



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Drops on unpatterned substrates

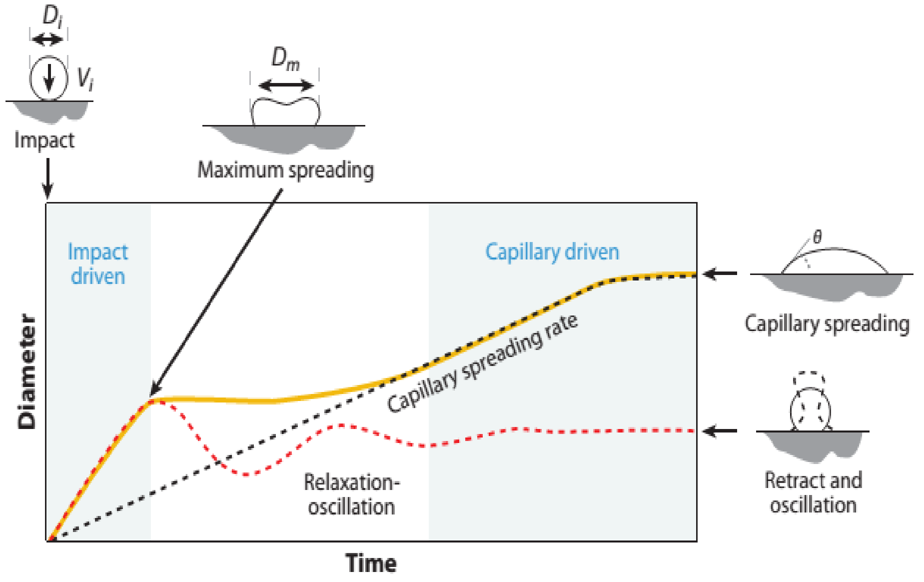
Derby, *Annu. Rev. Mater. Res.* 2010

Early stages:
kinetic effects

- Impact
- Spreading
- Recoil

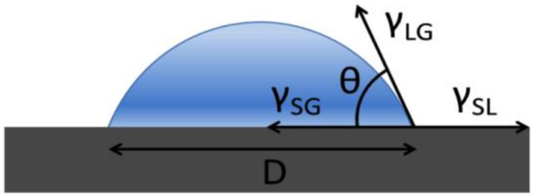
Late stages:
initial volume & capillarity

- Wetting
- Evaporation
- Solute deposition



Surface energy, Contact angle, Young-Dupré equation

- At drop triple line, 3 interfaces => 3 surface energies:
  - Interface solid liquid (ink)
  - Interface liquid gas (air)
  - Interface gas solid (substrate)



- Young-Dupré equation
  - Contact angle
- Changing the surface energy, e.g. by self-assembled monolayers (SAMs)
  - Change of the contact angle (Wettability property of the surface)

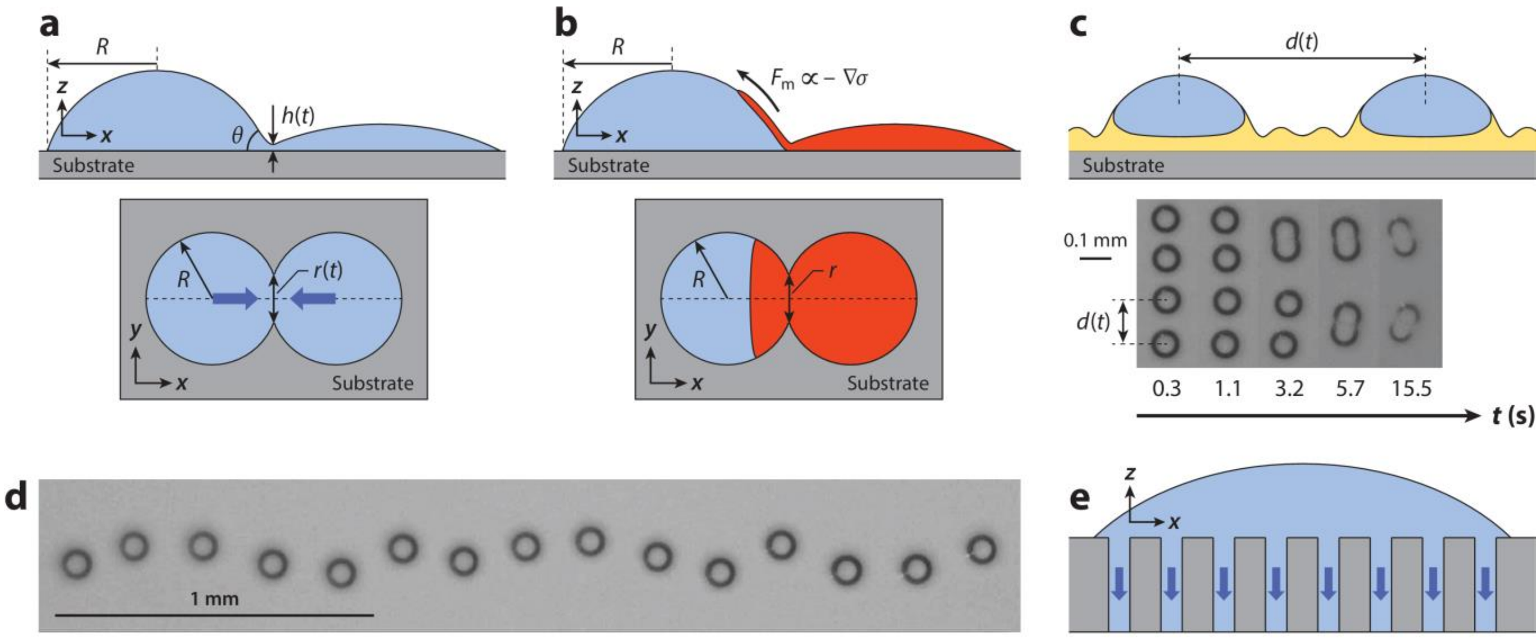
$$d_{con} = d_0 \sqrt[3]{\frac{8}{\tan\frac{\theta_{eqm}}{2}\left(3+\tan^2\frac{\theta_{eqm}}{2}\right)}}$$

$$\gamma_{LG}\cos\theta = \gamma_{SG} - \gamma_{SL}$$

$$\theta = \arccos\left(\frac{\gamma_{SG}-\gamma_{SL}}{\gamma_{LG}}\right)$$

$$\cos\theta_Y = \frac{\gamma_{SG}-\gamma_{SL}}{\gamma_{LG}}$$

Droplet merging



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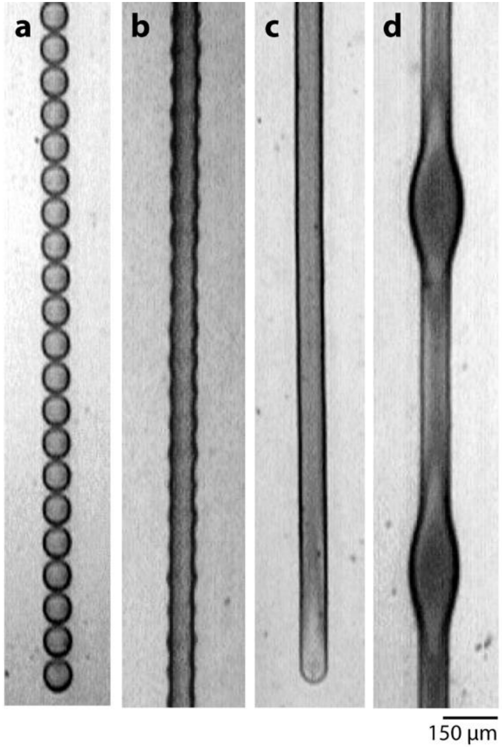
Drop spacing

a. Drop spacing is too large for drop coalescence
b. Initial coalescence leads to a liquid bead with a periodic irregularity
c. After sufficient overlap smooth sidewalls occur
d. If drop spacing is too small, a bulging instability forms

The critical spacing is a function of the print head traverse speed relative to the substrate.



Printed line behaviors

Morphology of the printed lines can change due to the temperature of the substrate and spacing between the neighboring droplets

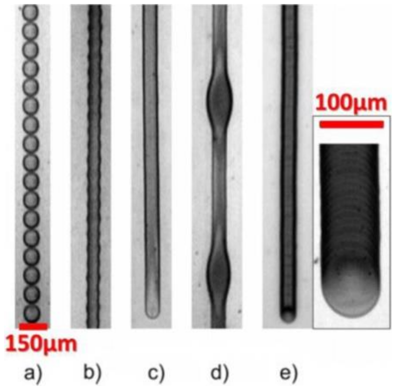
a) Individual drops
b) Scalloped
c) Uniform
d) Bulging
e) Stacked coins

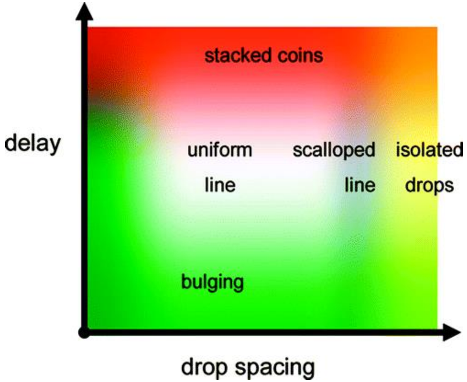
Trains of drops with pitches larger than final diameter do not coalesce.

Overlapping miscible drops coalesce into beads.

Contact line smoothing over time.

Too close drops induce bulges upon coalescence into beads.





S.-P. Chen et al. ECS J. Solid State Sci. Technol. 2015;4:P3026-P3033

Surface energy

Effect of surface energy

- Same volume of SU8 printed on Si and SAM-coated Si

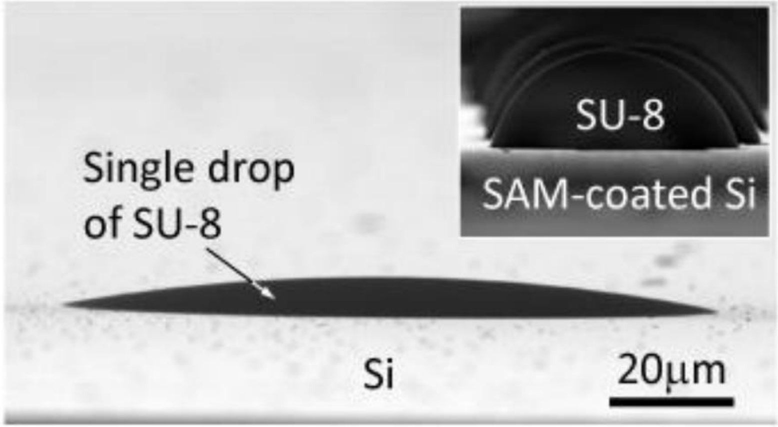
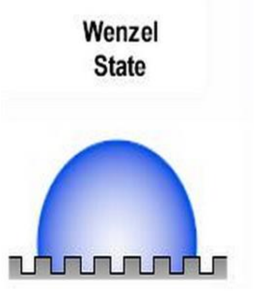


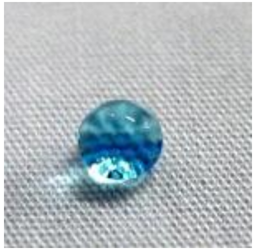
Figure 1-30. SEM images of a single drop deposited on silicon and an array of single drops on a SAM-coated silicon substrate (snapshot image).

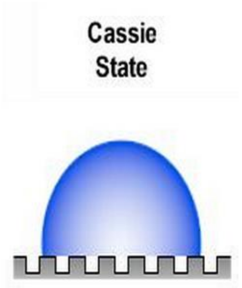
V. Fakhfouri, EPFL PhD thesis, 2008.

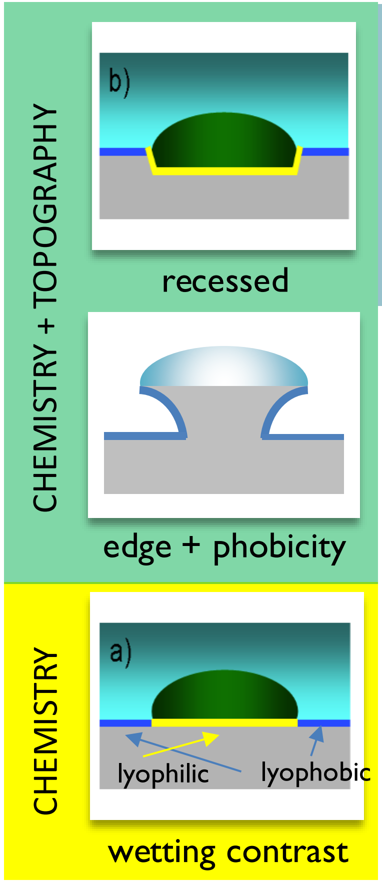
Surface energy & topography

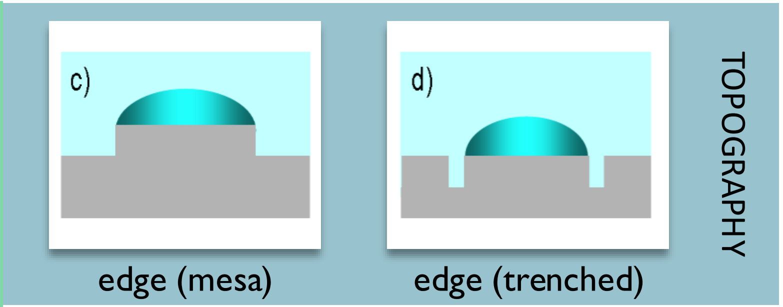
- Wenzel (1936): roughness amplifies chemical character
  - Hydrophilic surface → Roughness → More hydrophilic
  - Hydrophobic surface → Roughness → More hydrophobic
- Cassie-Baxter (1945): heterogeneous surfaces
  - Chemical heterogeneity & topography
  - Macroscopic properties are mean of microscopic properties
  - Air bubbles entrapped below liquid → fakir state
    - Superhydrophobic state (>150 deg)
    - topography + low surface energy



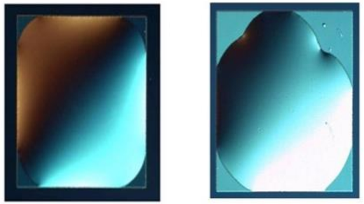


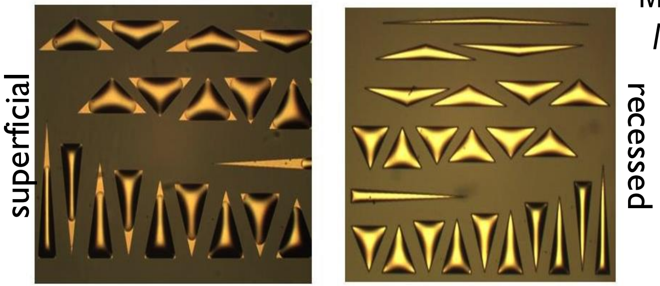






- ✓ Easy to fabricate
- • Almost conformal
- ▪ Sensitive to defects



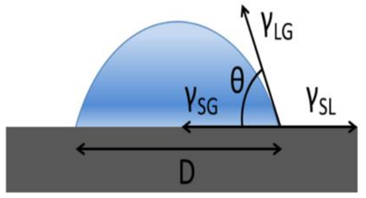


Mastrangeli *et al.*, *IEEE Trans.* 2011

Spherical shape by edge confinement

- Below the *capillary length* $\lambda = \sqrt{\frac{\gamma}{\rho g}}$
  - Young-Dupré equation → contact angle
  - Drop shape by surface tension only
  - Surface energy => γ_{SG} changes
  - Edge confinement

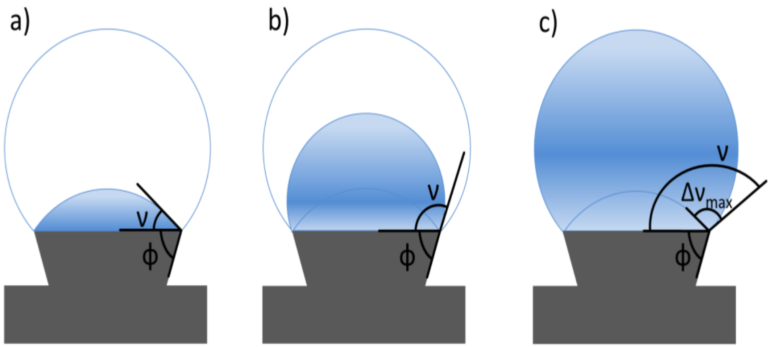
  (Gibbs' inequality, canthotaxis sector)



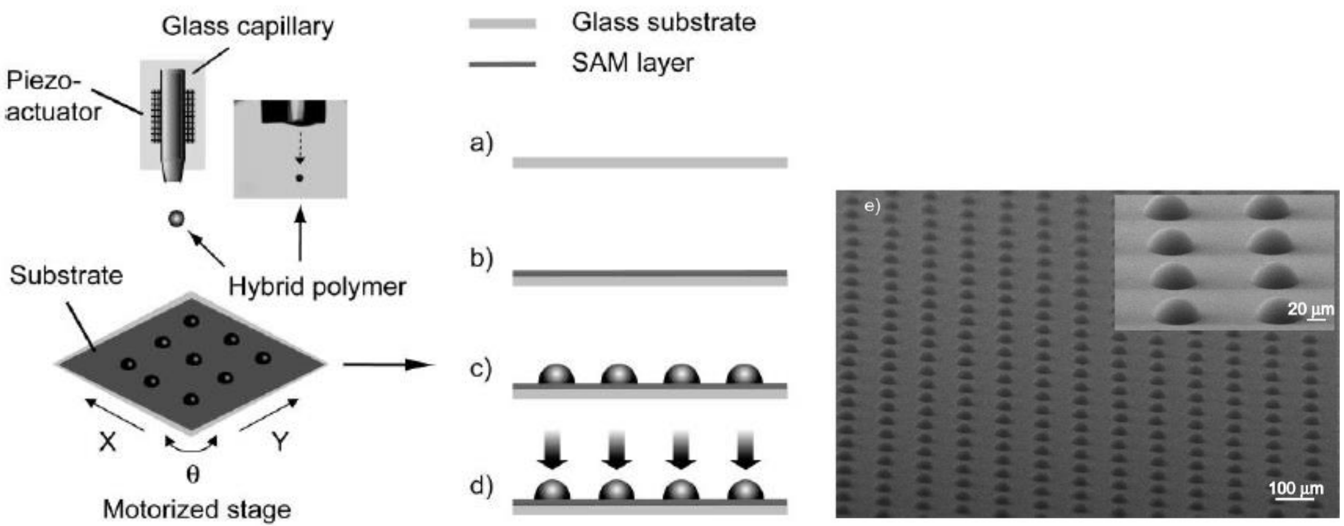
$$\theta = \arccos(\frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}})$$

$$\theta \leq \nu \leq \theta + \pi - \phi$$

θ : Contact
ν angle
ϕ : Edge angle
: Pinning

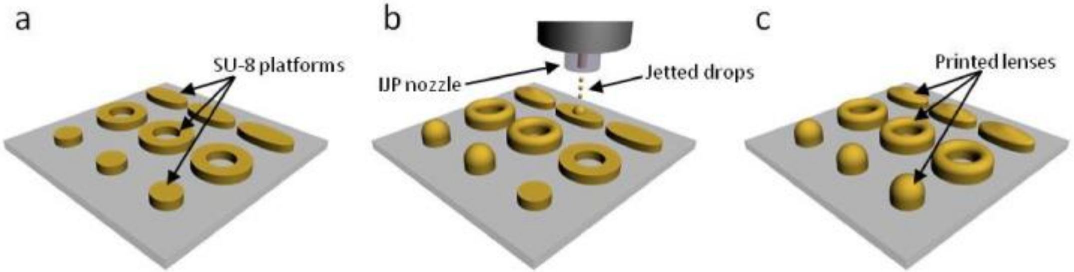


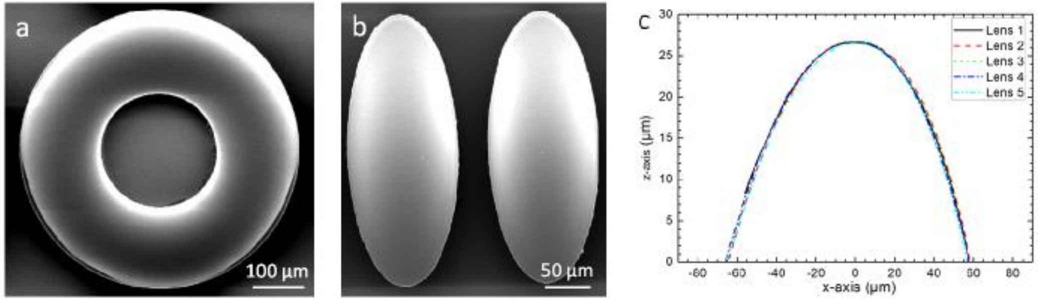
IJP of optical microlens array



Joo Yeon Kim et al. Opt. Mater. Express **1**, 259-269 (2011)

Microlenses with arbitrary shapes

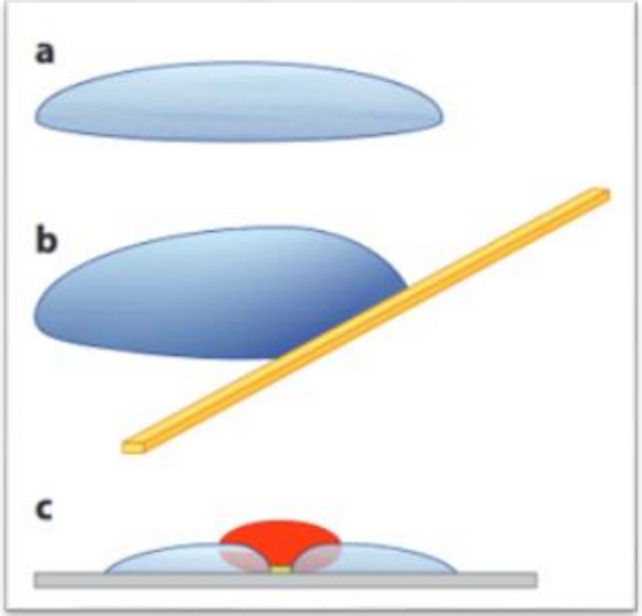




Cadarso, Opt. Express (2011)

Drops on patterned substrates

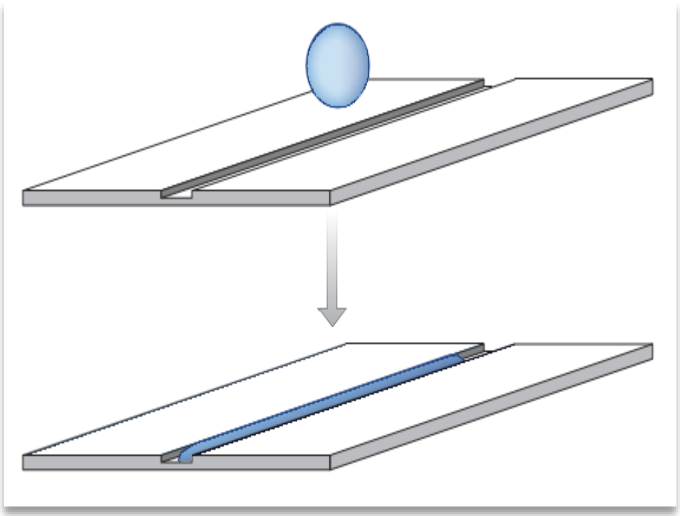
a. A droplet spread to its equilibrium configuration on a substrate
b. The presence of a fluid phobic stripe (yellow) will arrest spreading
c. A combination of two arrested drops defines the channel width between the source and drain beneath the gate for an all-polymer printed transistor



Derby,
Annu. Rev. Mater. Res. 2010

Drops in porous/channel surface

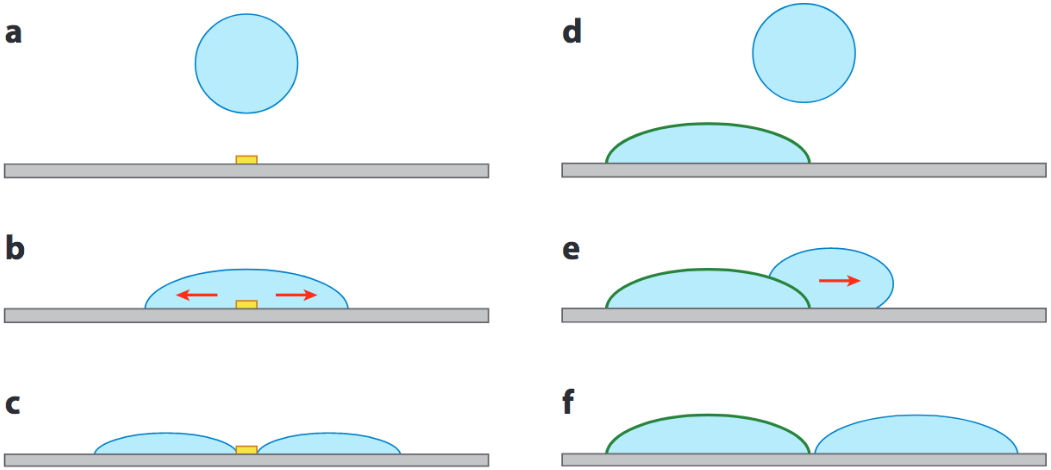
If a channel is cut or molded into a fluid-philic surface and subsequently a drop is deposited on the channel, the energetics of wetting will drive the fluid along the channel.



Derby,
Annu. Rev. Mater. Res. 2010

Drops on structured surface

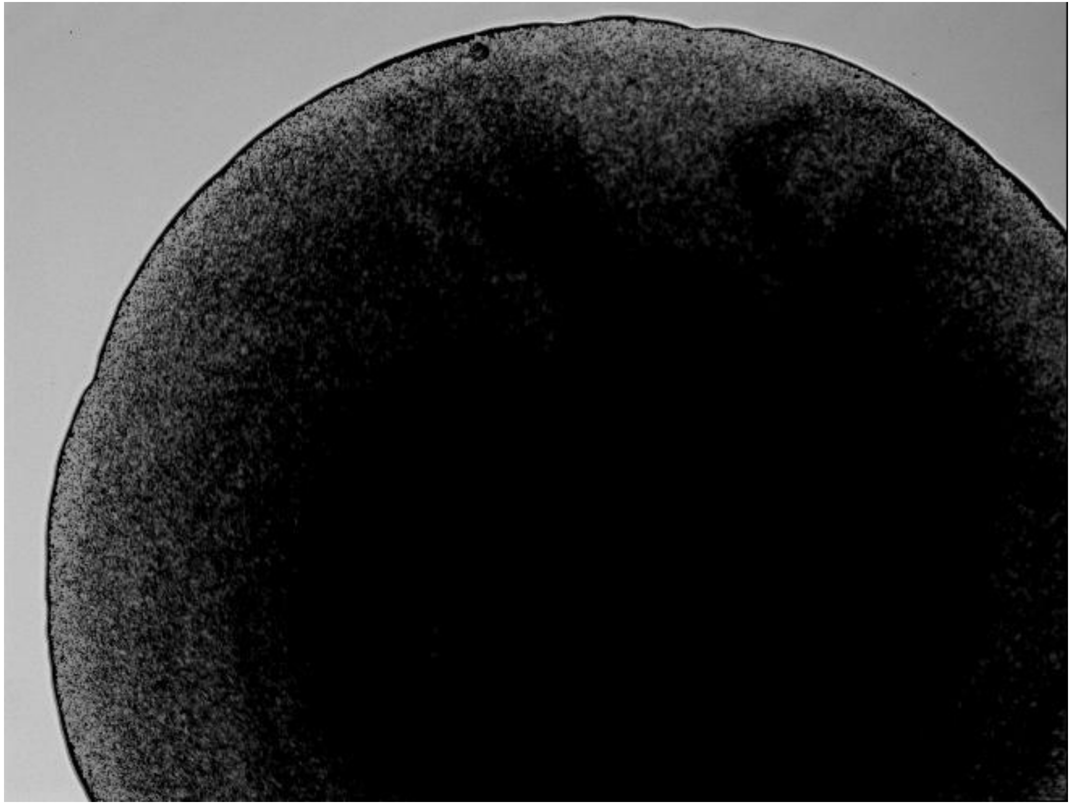
a. A fluid drop is printed onto a fluidphilic substrate above a fluidphobic stripe (yellow)
b. Fluid flow within the drop is driven by dewetting energetics
c. Final structure results in two drops separated by the narrow fluidphobic stripe
d. A polystyrene sulfonic acid (PEDOT) solution drop is printed onto a solidified PEDOT structure that has been plasma treated to generate a fluidphobic surface (green)
e. The second drop is driven from the surface of the initial drop by dewetting
f. 2 drops are separated by a narrow region after solidification



Derby,
Annu. Rev. Mater. Res. 2010

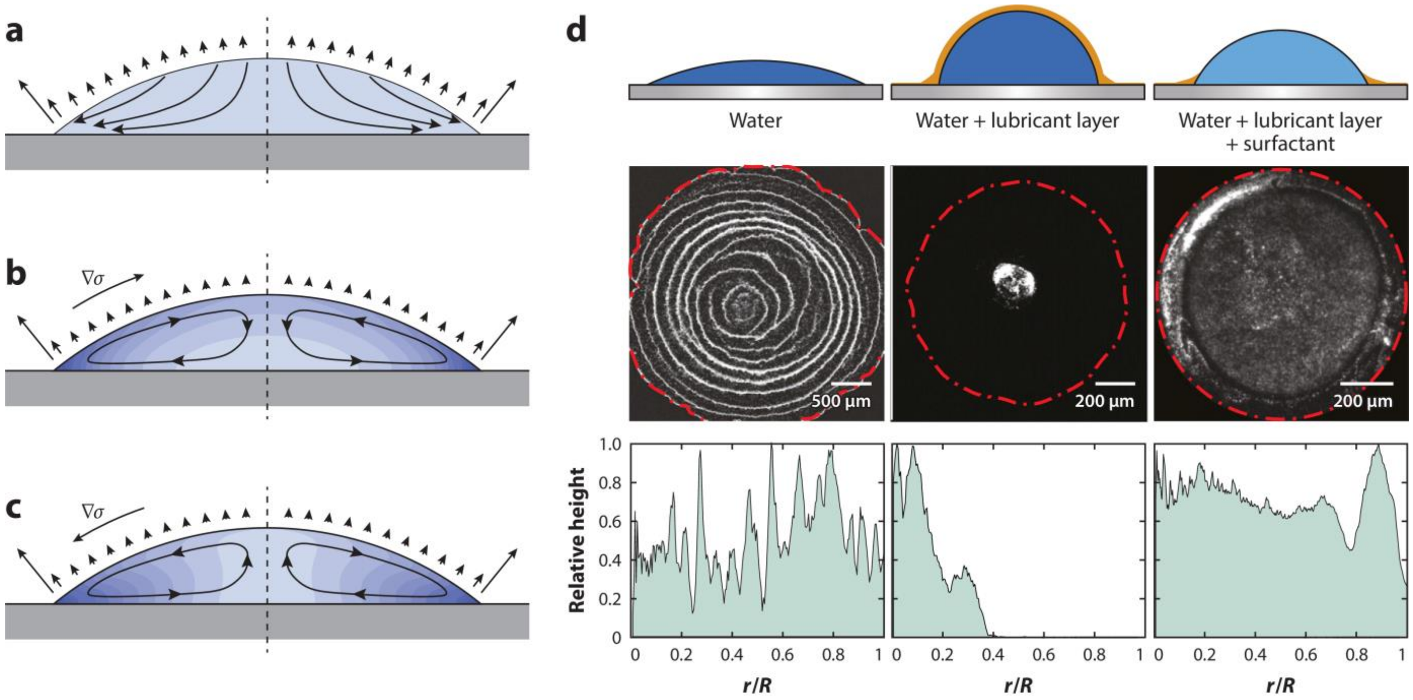
Droplet drying

Liquid assembly



Still *et al.*, *Langmuir* 2012

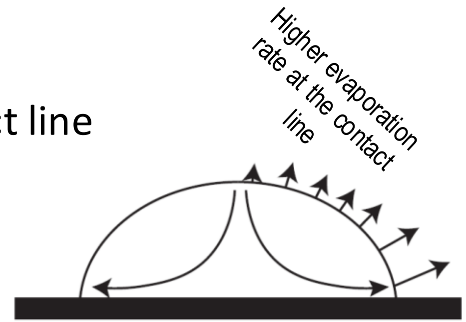
Droplet drying



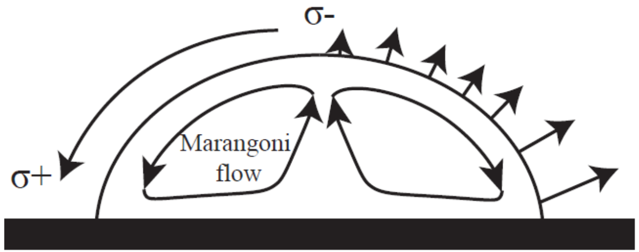
Lohse D. 2022
Annu. Rev. Fluid Mech. 54:349–82

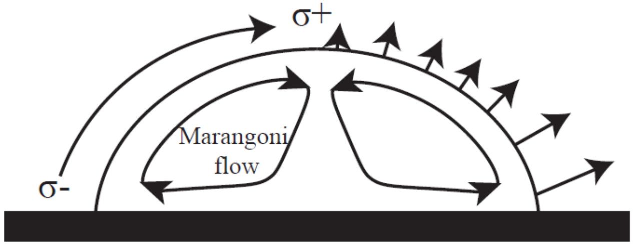
Droplet drying on a substrate

- Droplet containing single solvent
  - Higher evaporation rate at the contact line
  - Convection flow from the apex to the contact line

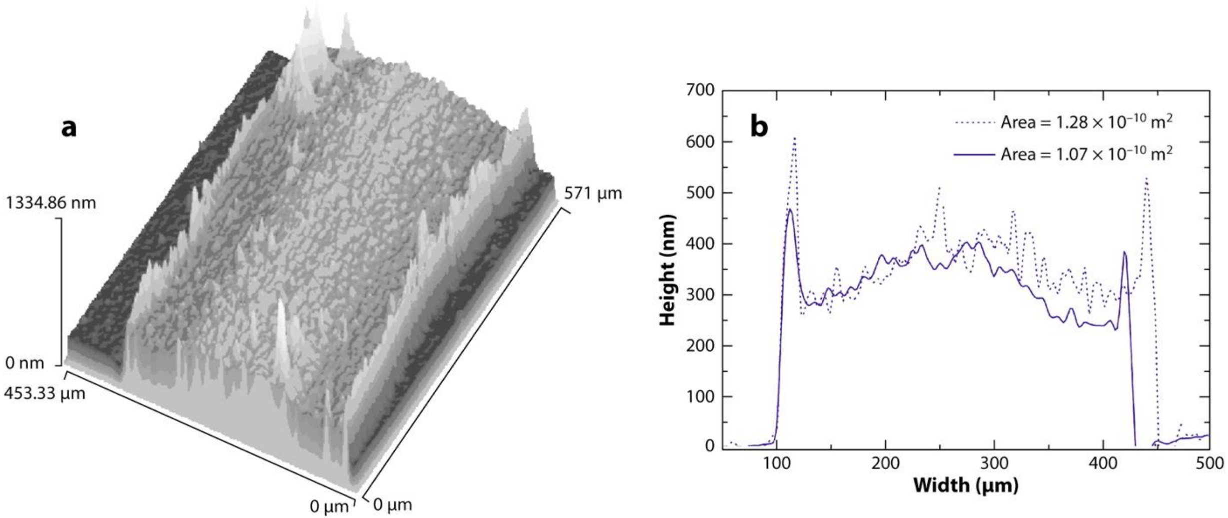


- Droplet containing mixture of solvents
  - Marangoni flow due to surface tension gradient





Track formation by IJP



(a) Interferometric image of a track formed from the drying of a liquid bead showing distinct ridges at the edges that have formed by fluid flow during drying.
(b) Two line profiles across the track showing the variation in height across the track.

Co-solvent strategy

Single solvent

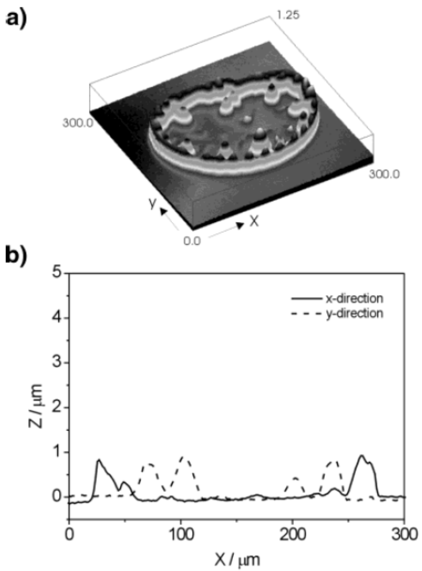


Figure 3. (a) Polymer dot, formed by a droplet of a 1 wt % solution of polystyrene in ethyl acetate on perfluorinated glass; (b) cross-sections in the *x*- and *y*-directions.

Mixed solvent

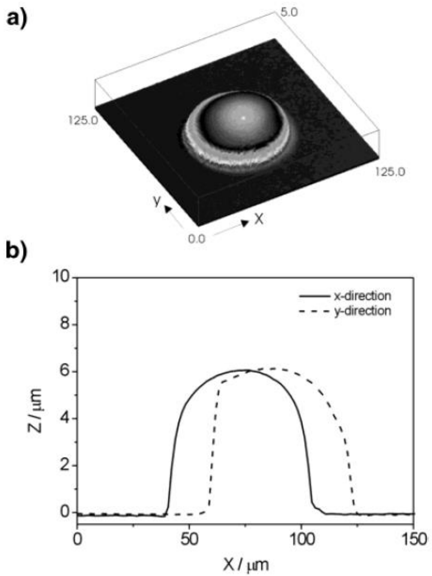


Figure 4. (a) Polymer dot, formed by a droplet of a 1 wt % solution of polystyrene in an 80/20 wt % ethyl acetate/acetophenone mixture on perfluorinated glass; (b) cross-sections in the *x*- and *y*-directions.

B. J. De Gans and U. S. Schubert, "Inkjet printing of well-defined polymer dots and arrays," *Langmuir*, vol. 20, no. 18, pp. 7789–7793, 2004.

Droplet drying with mixed solvent

- Mixed solvent (ethanol / water)

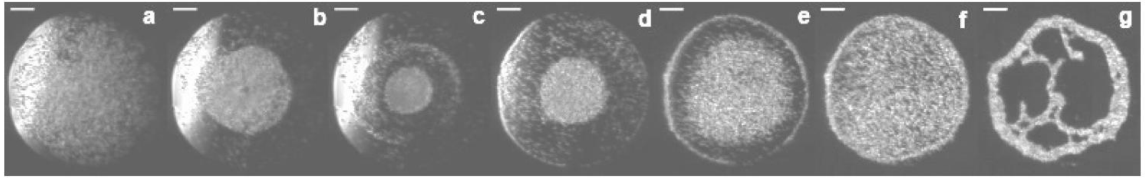


Figure 2. A droplet of 10%v ethanol/water containing 0.1%v 1-µm polystyrene spheres at a RH of 0.50 on uncoated glass. The group of particles that collects at the droplet center undergoes circulating Marangoni flow. Times normalized by the drying time, t_d, are a) 0.001 t_d, b) 0.05 t_d, c) 0.10 t_d, d) 0.51 t_d, e) 0.82 t_d, f) 0.92 t_d, g) 1.00 t_d. The drying time is 3.27 s. The scale bars are 50 µm

- Mixed solvent (methoxypropanol / water)

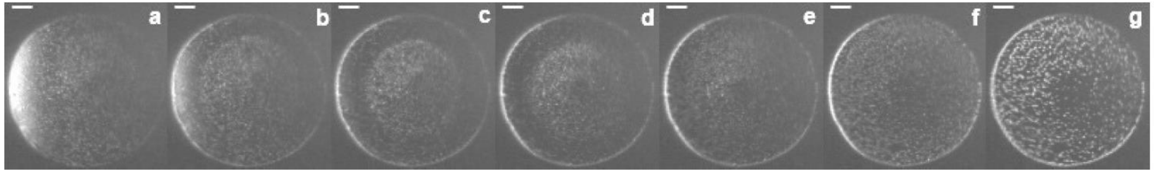


Figure 8. A droplet of 50%v PM/water containing 0.1%v 600 nm-polystyrene spheres at a RH of 0.65. Two regions of flow are apparent as drying progresses. An inner region of circulating flow and an outer region of radial flow. Times normalized by the drying time, t_d, are a) 0.15 t_d, b) 0.30 t_d, c) 0.44 t_d, d) 0.58 t_d, e) 0.73 t_d, f) 0.88 t_d, g) 1.00 t_d. The scale bars are 50 µm

Table 1. *Surface tensions, σ and vapor pressures, p, at 20°C [18].*

Fluid	σ / mNm^{-1}	p / kPa
Ethanol	22.4	5.95
Methoxypropanol	27.0	1.60
Water	72.9	2.34

E. L. Talbot, A. Berson, L. Yang, and C. D. Bain, *29Th Int. Conf. Digit. Print. Technol.*, vol. 44, no. July, pp. 307–312, 2013.

Summary of IJP

- Local deposition, quasi no-waste technique
- Cost-efficient & environment friendly
- Non-contact technique, flexible & non-flat substrates
- R2R compatible
- No cleanroom required
- Relatively affordable devices
- Large variety of material (inks)
  - Polymers, Organic solutions (e.g. biological fluids, cells), Inorganic solutions (e.g. nanocrystals, metal particles, solder)
- Serial process → Time consuming (multi-nozzle)
- Challenging control of droplets, nozzle clogging, drying effects, …

What you should know by now

- Understand continuous & drop-on-demand inkjet printing methods.
- Remember how to create single drops
- How drops are interacting with the substrate
- How drops are drying