Organic and Printed Electronics

LESSON 2/3 – PHYSICS AND TECHNOLOGY OF PRINTING

Prof. Vivek Subramanian

Why print?

- Low cost?

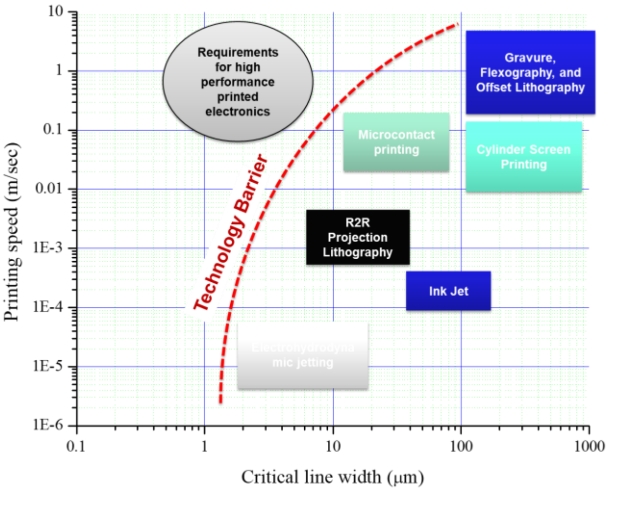
Courtesy:
G. Cho,
Sunchon National University

- Added functionality
  - Integration – spatially specific deposition
  - Customizability – digital printing
  - Lightweight / robust / flexible

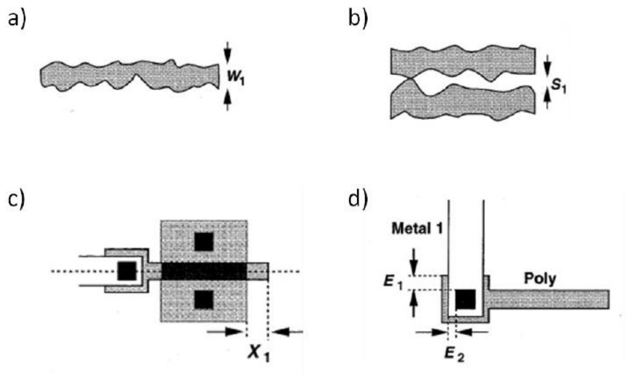
General tradeoffs in printing

- **Resolution: Printing techniques vary widely in resolution from nm (nanoimprint) to 100μm (high-speed screen)**
- **Speed: Traditional analog printing techniques (screen, gravure, offset) are exceedingly fast (100's of m/min), while nanoimprint is immature, and probably too slow for printed electronics**
- **Viscosity: Electronic materials often have limited viscosity ranges. Offset printing requires very high viscosity inks (like toothpaste), while digital techniques such as inkjet can work with low viscosities (e.g., alcohols)**

Resolution trade-offs in Printing



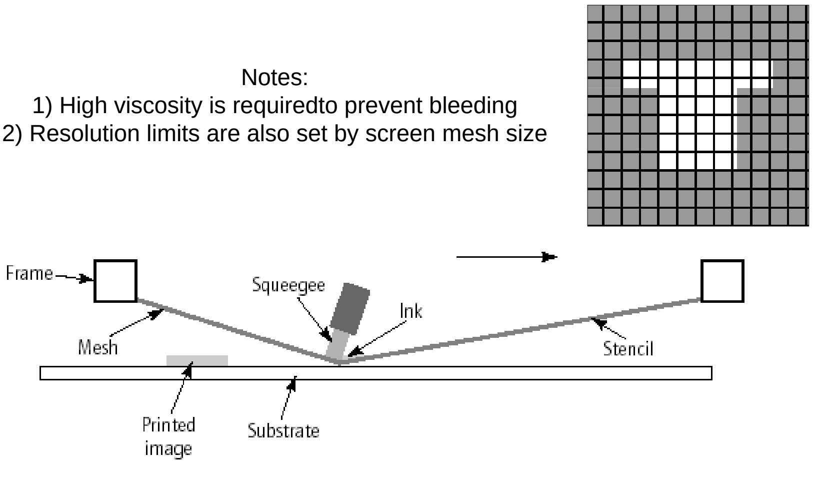
Pattern fidelity requirements



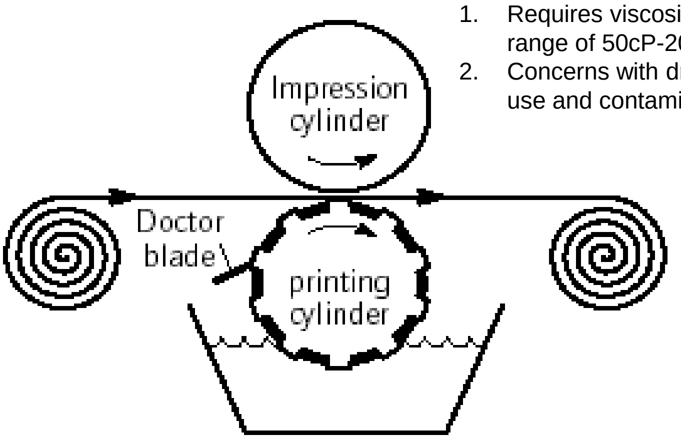
Consider:
- **Line edge roughness**
- **Line-space roughess**
- **Overlay**

Screen Printing

Notes:
1) High viscosity is requiredto prevent bleeding
2) Resolution limits are also set by screen mesh size

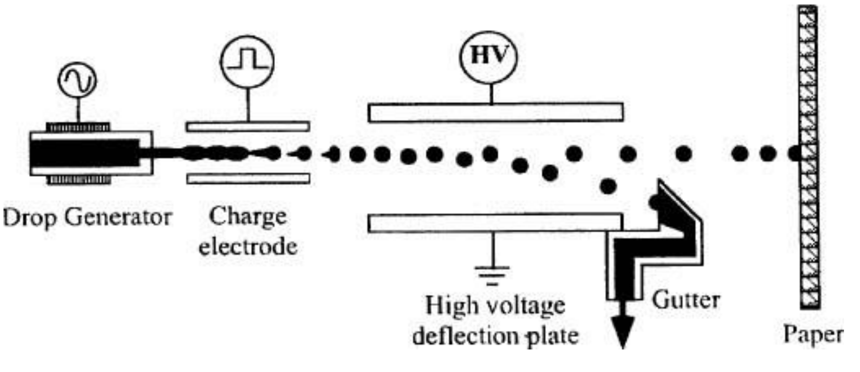


Gravure Printing



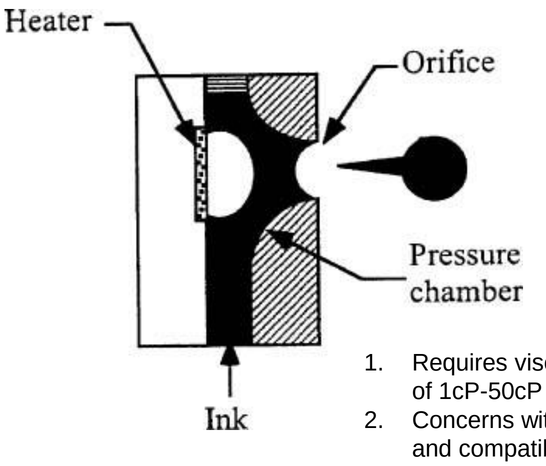
1. Requires viscosities in the range of 50cP-200cP
2. Concerns with drum re-use and contamination

Continuous Inkjet Printing



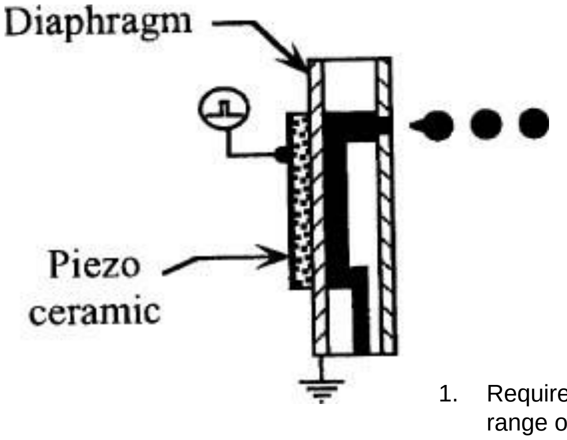
1. Requires viscosities in the range of 5cP-50cP
2. Concerns with ink wastage and contamination

Thermal Inkjet Printing



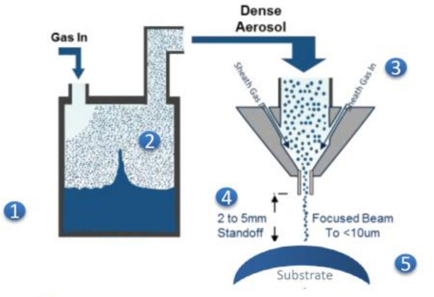
1. Requires viscosities in the range of 1cP-50cP
2. Concerns with ink degradation and compatibility

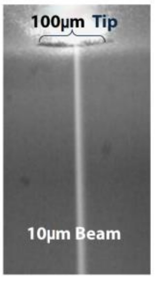
Piezo Inkjet Printing



1. Requires viscosities in the range of 1cP-50cP
2. Concerns with manufacturability

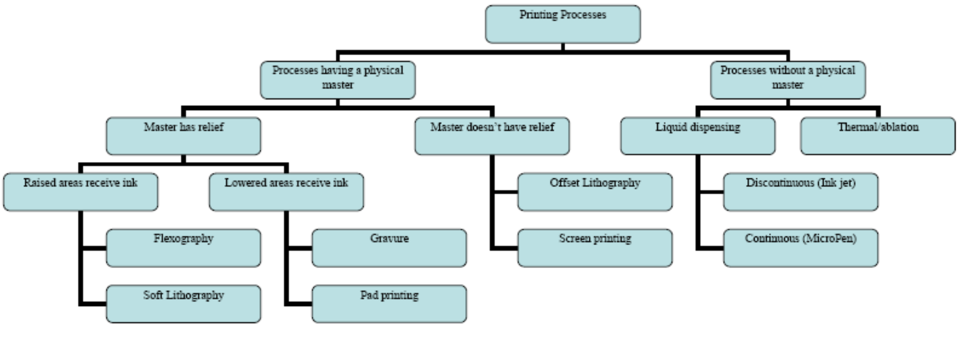
Aerosol jet





1. Atomize liquids: conductive inks, dielectric, (1-1,000 cP)
2. Mist of 1 to 5 um Ø highly dense, highly loaded droplets
3. Sheath gas surrounds and focuses particle beam
4. Continuous Flow Exits at 50m/s, remains collimated for up to 5 mm
5. Print on planar and non planar substrates

Taxonomy of printing processes

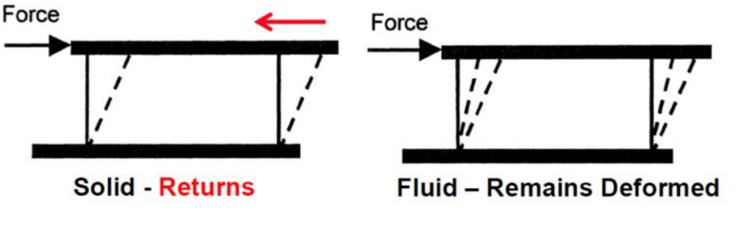


Choosing a print technique

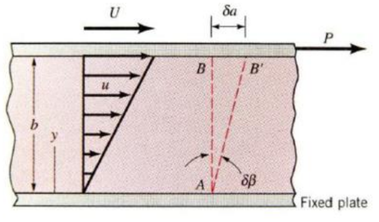
- **Materials Properties**
  - Viscosity
  - Surface Tension
- **Physical Requirements**
  - Resolution
  - Registration
  - Thickness
- **Economics**
  - Throughput
  - Master / Plate costs
  - Waste
  - Material Costs

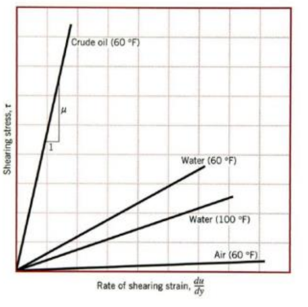
What is a fluid

- A fluid is any substance that deforms continuously under the application of shear stress of any magnitude
- Gasses and liquids
- Newtonian liquid



Viscosity





$$\tau = \mu \frac{du}{dy}$$

where
τ is the shearing stress
μ is the absolute dynamic viscosity
$\frac{du}{dy}$ is the velocity gradient

In addition:

$$\mu \sim \mu_0 e^{-(T-T_0)}$$

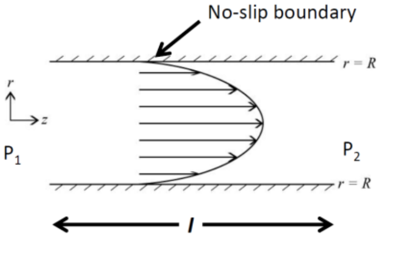
Thermal effects

Fluid flow through a pipe

Poiseuille's equation and scaling

For a fluid passing through a tube, the Naiver-stokes equation implies

$$V = \frac{\pi (P_1 - P_2) r^4}{8 \mu l}$$



For narrow pipes the flow rate (V) is strongly reduced.

Household pipes
ΔP=3 bar, R=5 cm
μ= 0.01 poise, L = 10m
V= 73 m/s

Washing machine
ΔP=3 bar, R=1 cm
μ= 0.01 poise, L = 5 m
V= 0.2 m/s

Ink-jet printer
ΔP=3 bar, R=100 μm
μ= 0.01 poise, L = 5 cm
V= 20 μm/s

The Reynolds number

- The Reynolds number is a ratio between the internal forces in a fluid and the viscous forces

$$Re = \frac{\rho V D}{\mu}$$

Where
ρ is the fluid density
V is the fluid velocity
D is the pipe diameter
μ is the viscosity

Re < 2100
- Laminar (Stokes) flow
- Slow fluid flow
- No inertial effects
- Heavy damping

Re > 4000
- Unstable laminar flow
- Turbulent flow

Osborne Reynolds
Born Belfast 1842
First UK "Professor of Engineering"

The Reynolds number in inkjet printing

Household pipes	Washing machine	Ink-jet printer
ΔP=3 bar, R=5 cm	ΔP=3 bar, R=1 cm	ΔP=3 bar, R=100 μm
μ= 0.01 poise, L = 10m	μ= 0.01 poise, L = 5 m	μ= 0.01 poise, L = 5 cm
V= 73 m/s	V= 0.2 m/s	V= 20 μm/s

Water density = 10^3 kg.m^3
Viscosity = 10^{-3} kg.s^{-1}.m^{-1}

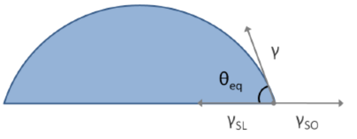
Re=3.65 x 10^6	Re=2000	Re=2 x 10^{-4}

- For most flow rates and small pipes Re is small and the flow is laminar
- Viscosity is dominant and we are in the realm of Microfluidics!

Liquids on surfaces: Some basic discussion

$$\gamma \cos \theta_{eq} = \gamma_{SL} - \gamma_{SO} \quad (1)$$

The fluid's surface tension is γ, and γ_{SL} and γ_{SO} represent the substrate-liquid and substrate-air interfacial tensions, respectively



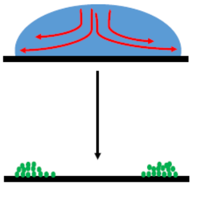
The substrates in this work are rough and have defects, and the printed inks dry and deposit solute. For both of these reasons, the contact line's advancing (θ_{adv}) and receding (θ_{rec}) contact angle separate in value leading to contact-angle hysteresis. The contact line is stable when $\theta_{rec} < \theta < \theta_{adv}$, else it retreats or advances as appropriate. Evaporating colloidal inks often have zero retreating contact angle and are said to have pinned contact lines that may advance but never retreat.

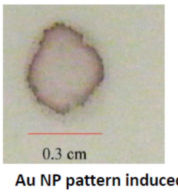
Effects with real inks

"Coffee Ring" Effect and Marangoni Flow

- During solution evaporation, there are two major competing evaporation-driven effects, "coffee ring" effect and Marangoni flow.

"Coffee ring" Effect

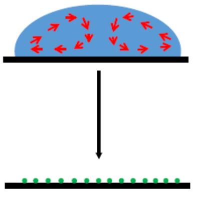


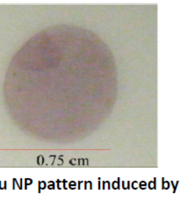


Au NP pattern induced by "coffee ring" effect

Dense, ring-like structure along the perimeter
1) Absence of circulating flow
2) Contact line of drying droplet is pinned
3) Outward flow carries solutes to the periphery

Marangoni Flow

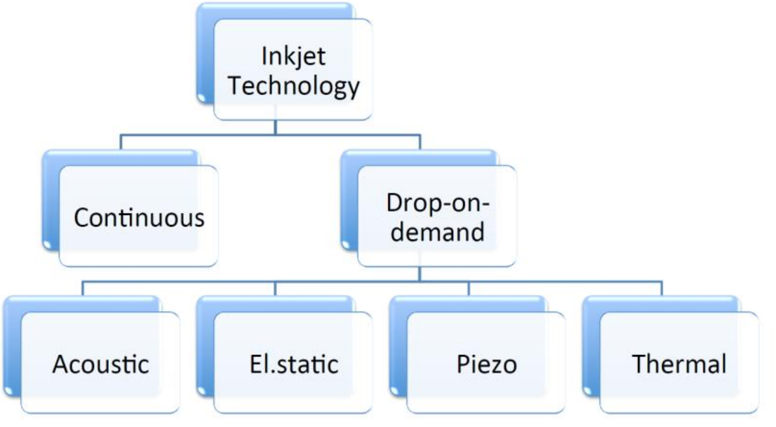




Au NP pattern induced by Marangoni flow

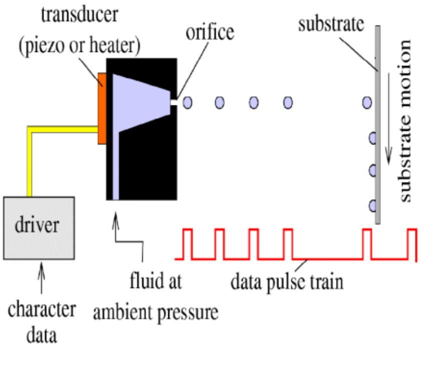
Ordered structure across the surface
The surface tension driven flow carries particles inward toward the top of the droplet and then plunges them downward where they can either adsorb onto the substrate near the center of the droplet or be carried along the substrate to the edge, where they are re-circulated along the free surface back toward the top of the droplet.

Taxonomy of major inkjet technologies



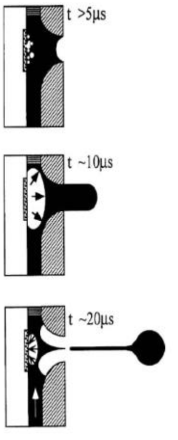
Droplets on demand inkjet printing

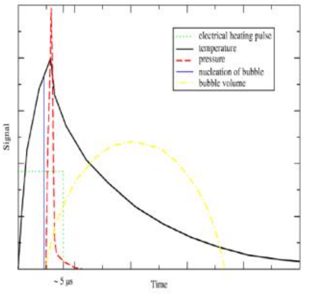
- Mechanism of droplet formation:
  - Thermal
  - Piezo-electric
  - Electrostatic
  - Acoustic

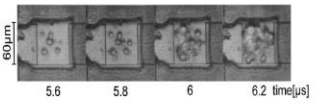


Thermal inkjet printing

- Phase of droplet formation
- Heating
  - Overheated ink (over the spinodal limit, around 300°C for water)
  - At 300°C: nucleation of bubble
- Expansion
  - Ejection of ink
  - Parallel to bubble expansion
- Droplet formation
  - Collapsing vapour bubble
  - Retraction of bulk ink
  - Refilling of cavity (80-200 us, speed critical step)

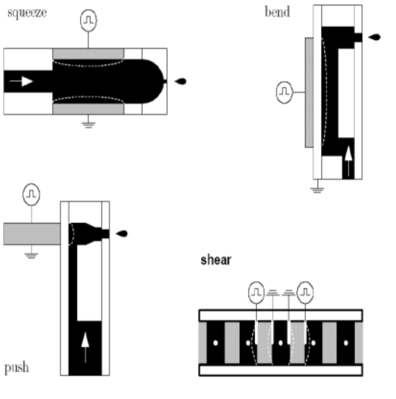




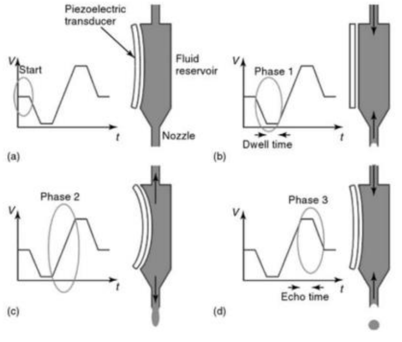


Piezo inkjet printing

- Deformation of piezo-ceramics
- Change in volume
- Pressure wave propagates to nozzle
- Deflection of piezo-ceramics in submicrometric range
- Piezo-element has to be much larger than orifice
- Main problem: miniaturization



Droplet formation in piezoelectric inkjet printers



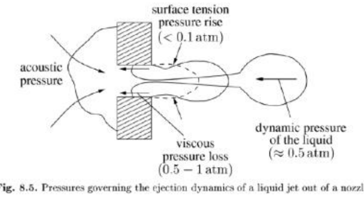
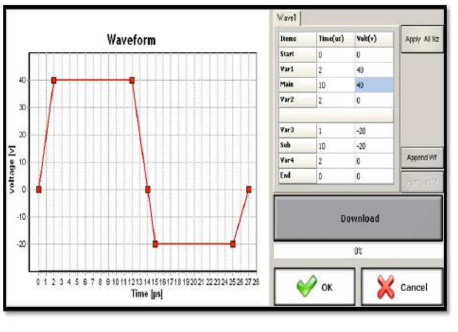
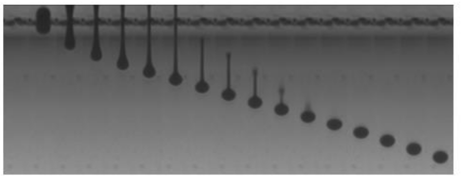


Fig. 8.5. Pressures governing the ejection dynamics of a liquid jet out of a nozzle

a) Starting deflection
b) Ink influx & meniscus formation
c) Acoustic -> kinetic energy
   high velocity jet from nozzle
   - Viscous pressure loss
   - Negative pressure wave reflection
   - Drop formation
d) Cavity relaxation period & meniscus formation

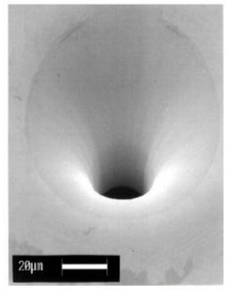
Example: typical bipolar waveform



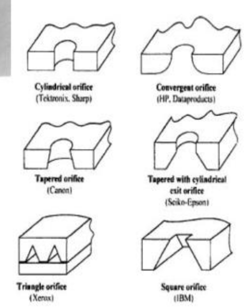


Nozzle design

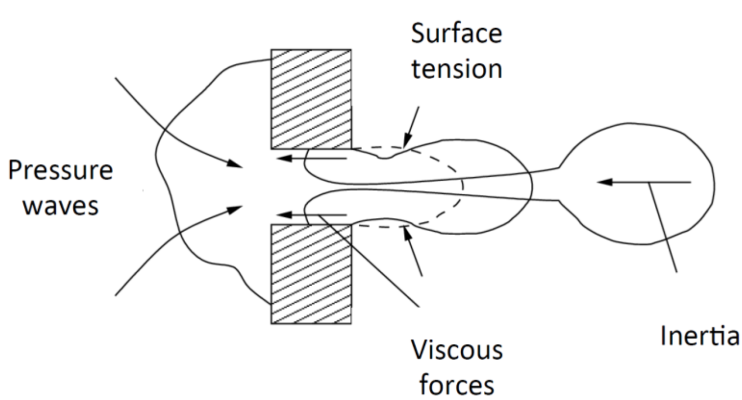
- Geometry parameters of nozzle
  - Diameter
  - Depth
- Effect on droplets
  - Volume
  - Speed
  - Deflection angle
- Effect on ink supply (refilling)
  - Capillary forces
- Fabrication tolerances limit picture quality
- Fabrication of orifice plates
  - Laser-ablation in polyimide, especially for small nozzles (10 pl, 20 um)
  - Nickel-electroplating
  - Electro-discharge machining (EDM)
  - Micro-punching
  - Micro pressing



Electroplated Ni-nozzle



Ink design considerations



Ink formulation

The weber number relates the balance between inertial and capillary forces in a fluid

$$We = \frac{\rho V^2 D}{\gamma}$$

Where
ρ is the fluid density
V is the fluid velocity
D is the pipe diameter
γ is the surface tension

The Ohnesorge number is the ratio of the Reynolds and Webber numbers

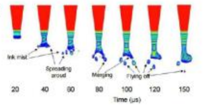
$$Oh = \frac{We^{1/2}}{Re}$$

Inverse ratio gives the Z index for inks

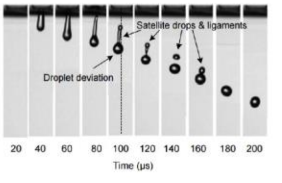
$$Z = Oh^{-1} = \frac{(D\rho\gamma)^{1/2}}{\mu}$$

Numerical criteria for ink formulation

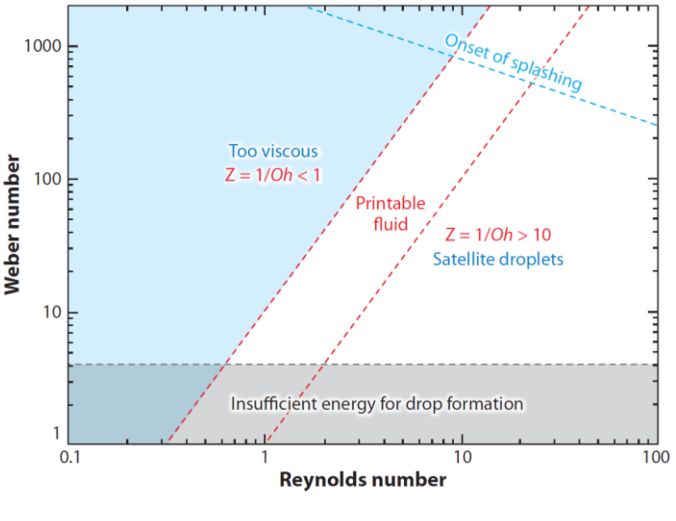
Z > 2 for successful printing
Viscosity large enough to dissipate acoustic-> kinetic shock



Z < 70
Satellite Droplets form separately to the main drop

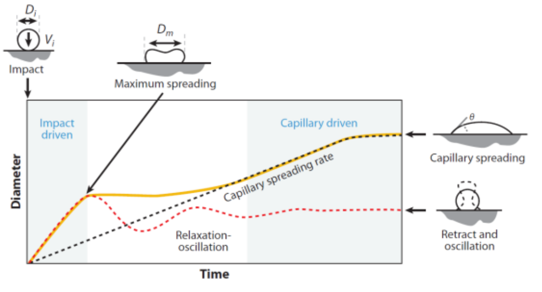


Drop ejection



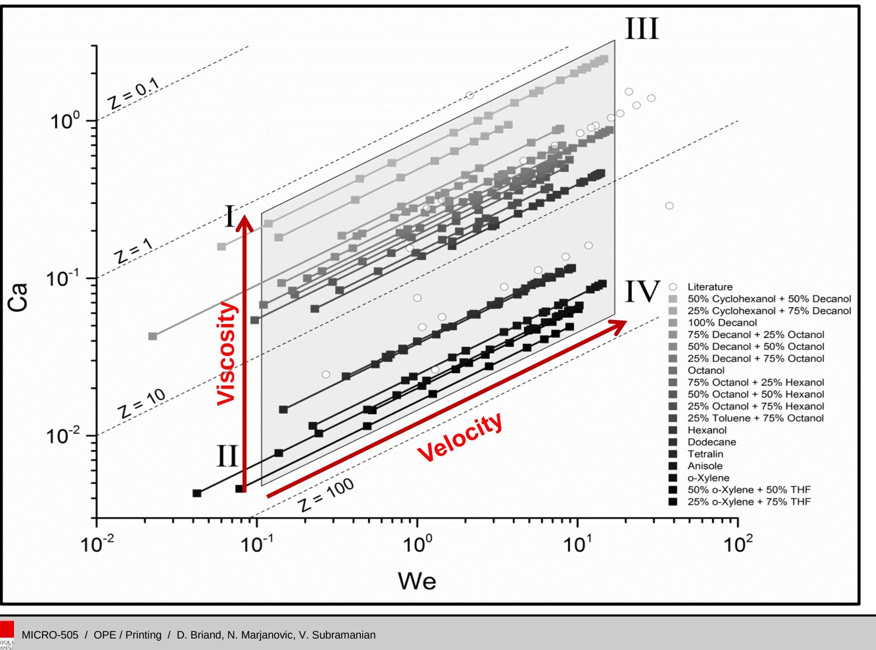
On the surface

Physics of drop: impact

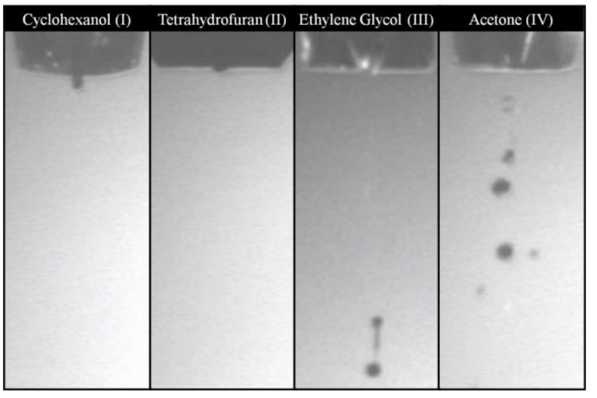


- The final diameters is a linear function D_i
- The drop footprint increases with decreasing the contact angle and is about $3D_i$ at a contact angle of 10°
- Coffee ring effect

Jettability Window



Breakdown Mechanisms Observed

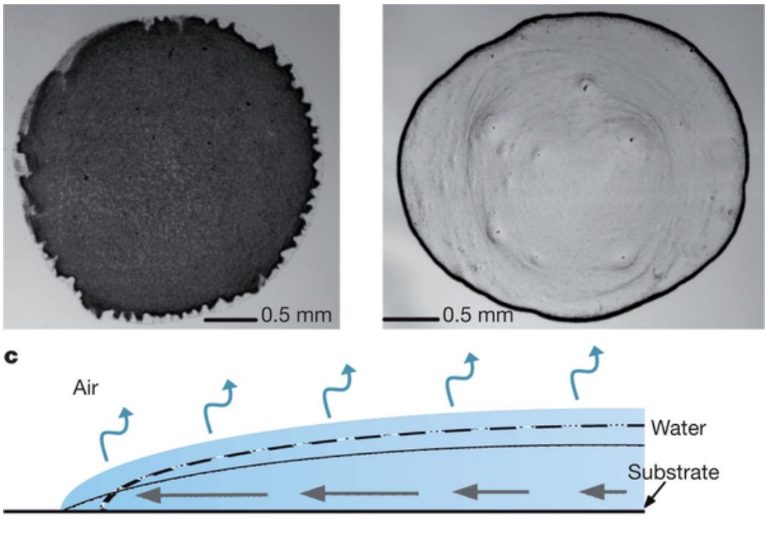


Regions I and II:
- intertial force (driven by pulse amplitude) too low for drop ejection

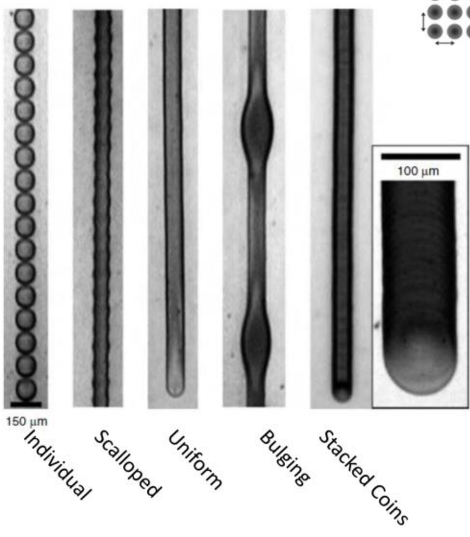
Region III:
- emerging ink pillar too long → satellite drops form from tail of drop

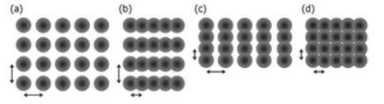
Revion IV:
- inviscid ink subjected to large intertial force → wavelike instability created → multiple breakups of drop tail

Reminder: the coffee ring effect



Pattern formation





- Patterns of dots
- Dot spacing

Wetting

$$\gamma \cos(\theta_{eq}) = \gamma_{SL} - \gamma_{LG}$$

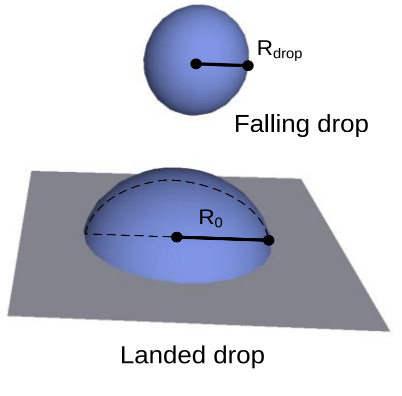
Drying effects

Substrate choice

γ_{ink} < Substrate surface energy
- Coating
- Functionalizing

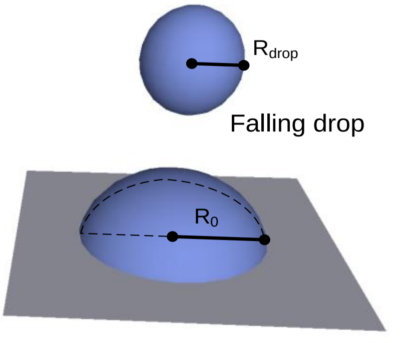
So what causes these effects?

- **Step 1: Drop hits the surface and expands to an impinging radius Ro**



So what causes these effects?

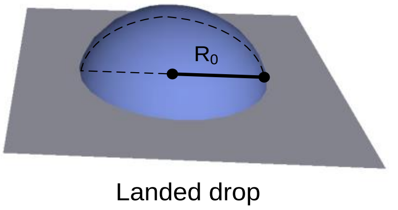
- Step 2: Edge of drop is "pinned"



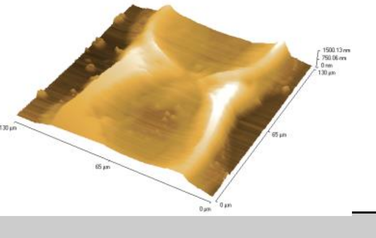
Landed drop

So what causes these effects?

- **Step 3: In isolated drops, drying causes:**
  - **Convective flow: edge is cooler than center, causing outward flow of material (coffee ring effect)**
  - **Marangoni effect: surface tension is temperature dependent, causing flow of material (can reverse coffee ring effect).**
  - **Final structure depends on relative rates**

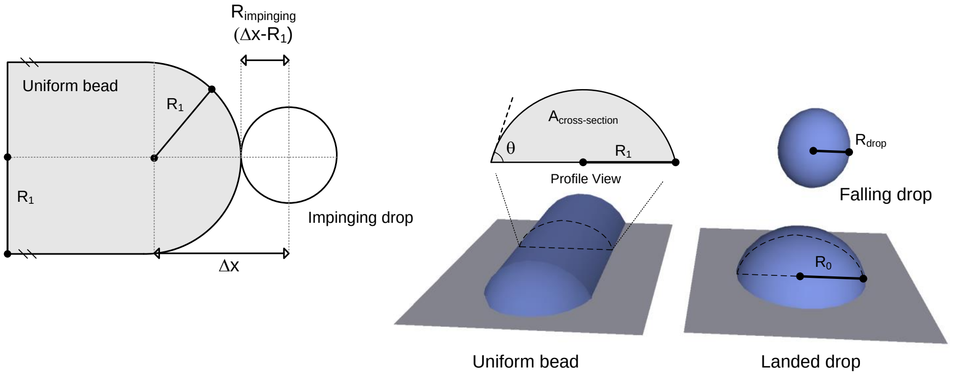


Landed drop



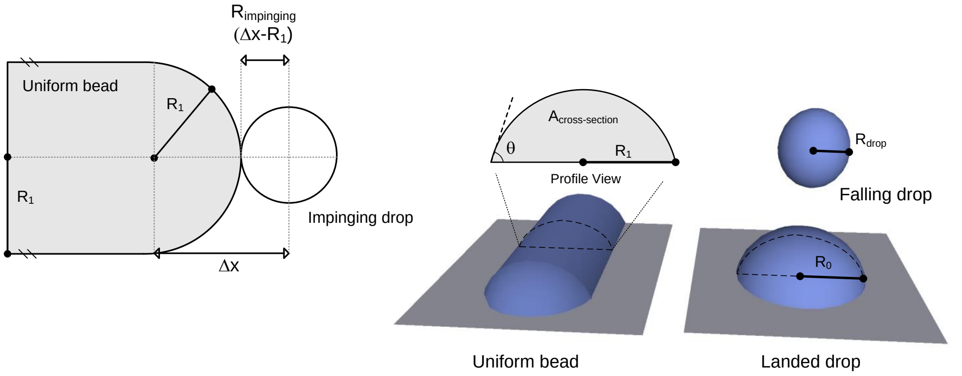
What happens in lines?

- **Step 1: Impinging drop "connects" to bead of line, and material flows back into line for same reason that coffee ring occurs**



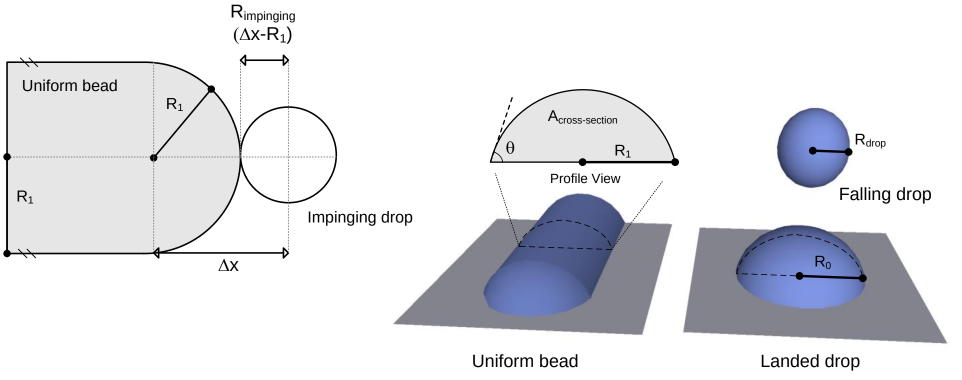
What happens in lines?

- **If flow is too slow, drop "dries" before line evens out, causing scalloping**

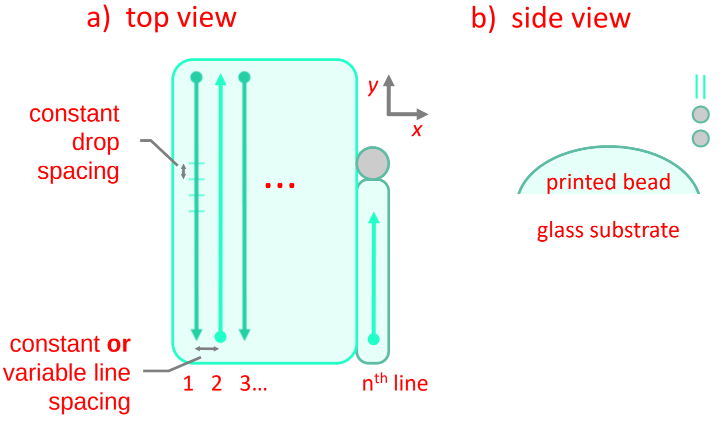


What happens in lines?

- **If flow is too fast, bead cannot absorb material fast enough, causing bulging**



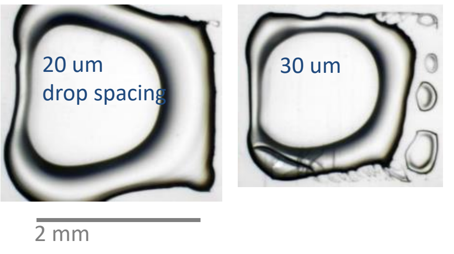
Two dimensional shape generation

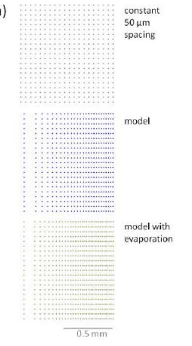


- **As patterns are printed, the contact angle of the bead can go in and out of the steady-state zone… this leads to instabilities**

Bulging and instability in two dimensions

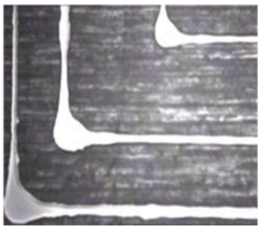
- **Dense drops cause bulging**
- **Sparse drops cause bead separation (since bead contact angle drops below receding contact angle)**

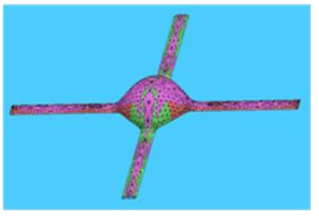


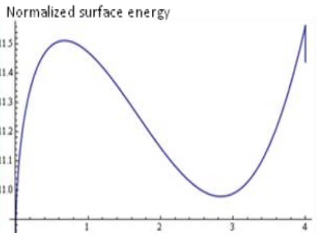


- **There is therefore an inherent limit to constant-space printing, which is what *all* existing tools tend to do.**
- **Solution: adjust drop spacing to control stability**

Instabilities in corners



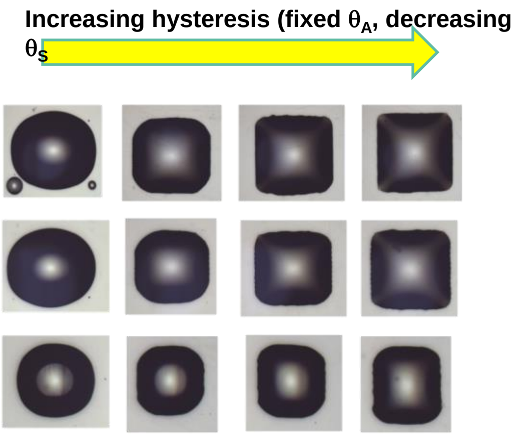




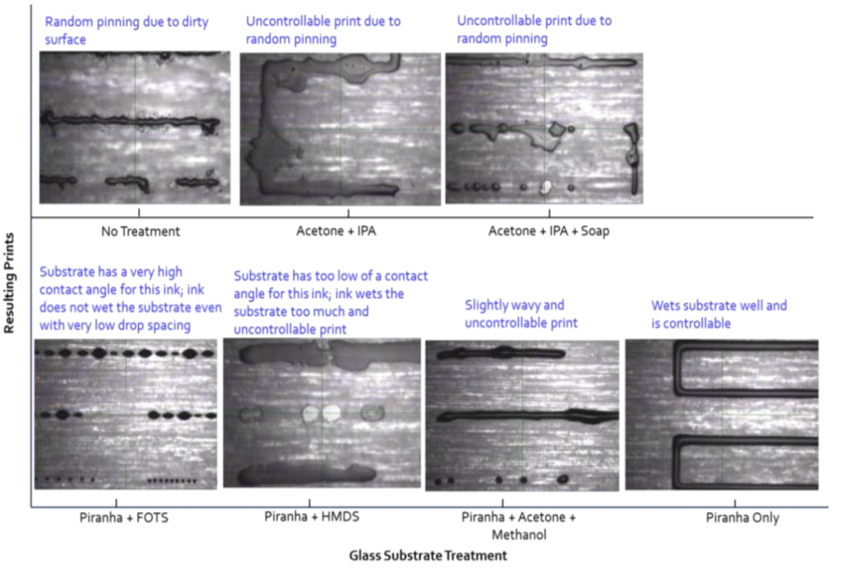
- **Flow in corners can drive to formation of bulges**
  - **Can position to equilibrium that eliminates bulges by proper design of process**
  - **Can exploit bulge formation to cause linewidth shrinking… (more on this later)**

The impact of the substrate

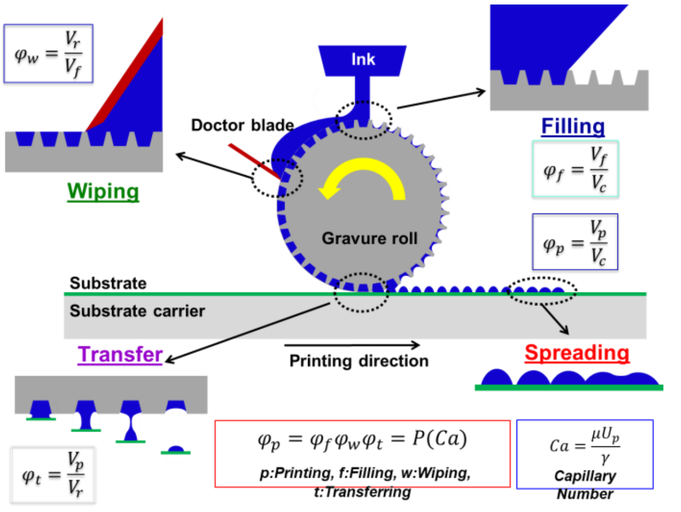
- **E.g., controlled contact angle hysteresis**



Substrate Interactions

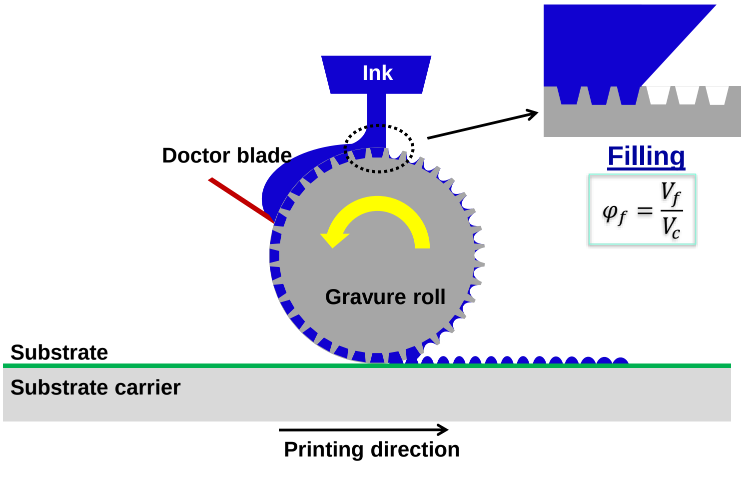


Gravure Printing

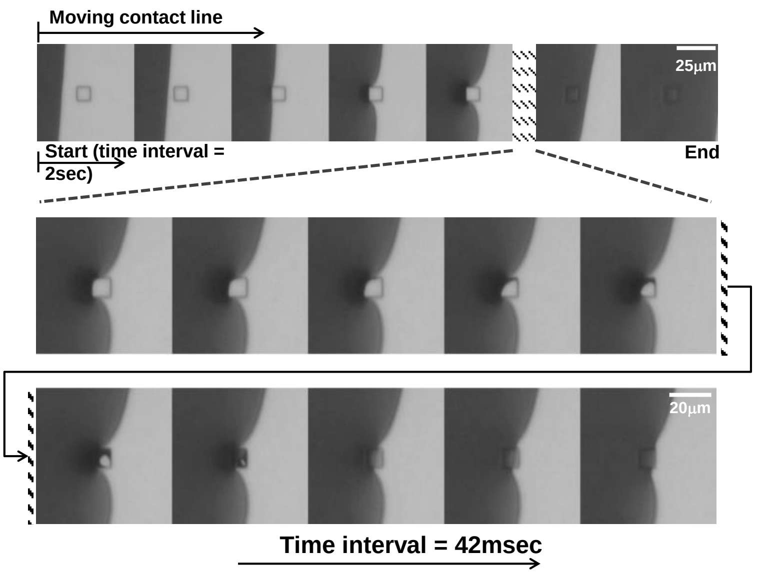


Kitsomboonloha, R., Morris, S. J. S., Rong, X., & Subramanian, V. (2012) *Langmuir*, *28*(48), 16711–23

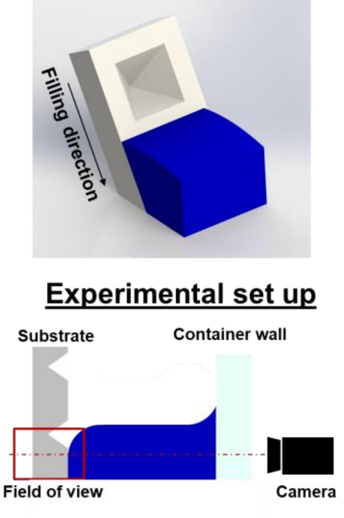
Filling Process

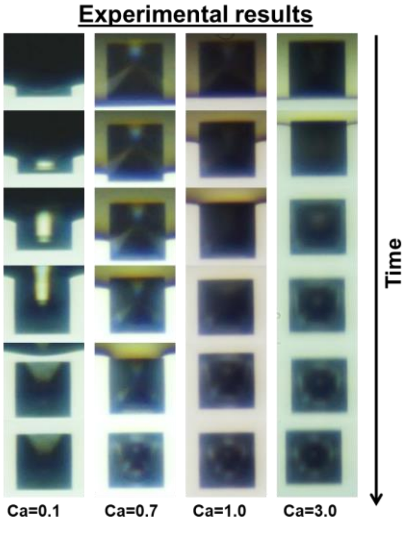


Filling Mechanism

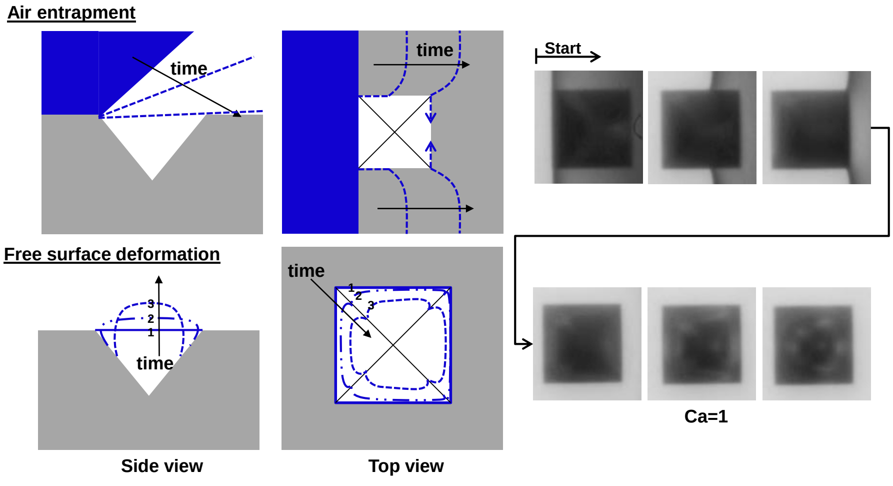


Filling Mechanism



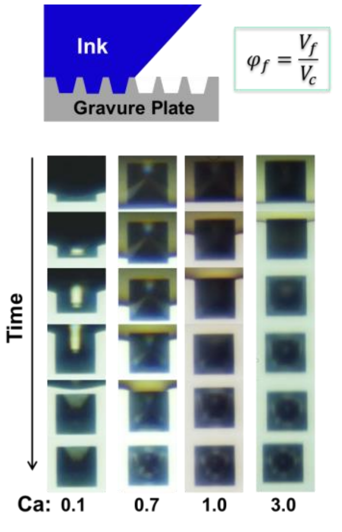


Air entrapment

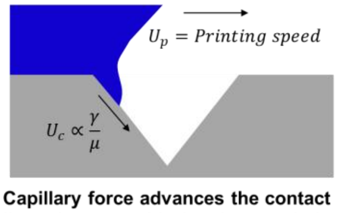


Assume prefect pinning at the cell edges

Filled Volume Fraction

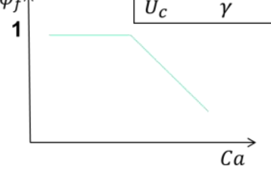


$$\varphi_f = \frac{V_f}{V_c}$$



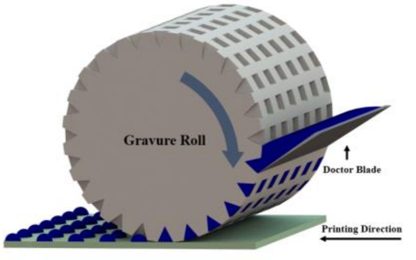
Capillary force advances the contact line advances with the characteristic velocity.*

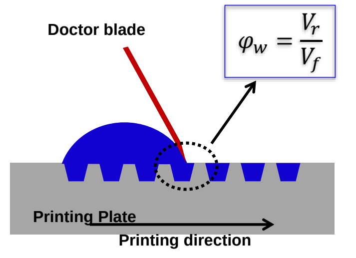
$$\frac{U_p}{U_c} = \frac{\mu U_p}{\gamma} = Ca$$

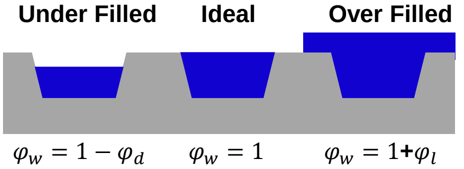


* Gennes, P. D.; Brochard-Wyart, F.; Quere, D. ,Springer, 2004.

Wiping Process



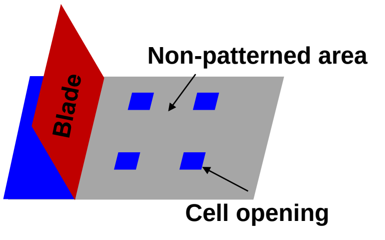




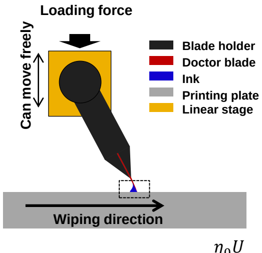
$\varphi_w = 1 - \varphi_d$ $\varphi_w = 1$ $\varphi_w = 1 + \varphi_l$

φ_d = Drag-out volume fraction

φ_l = Lubrication film volume fraction

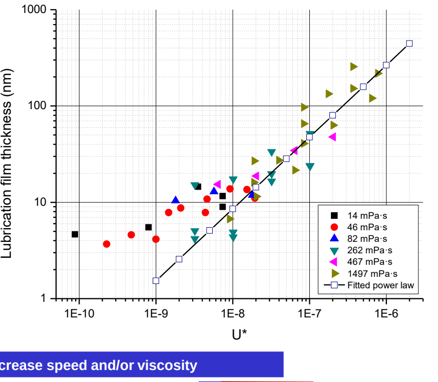


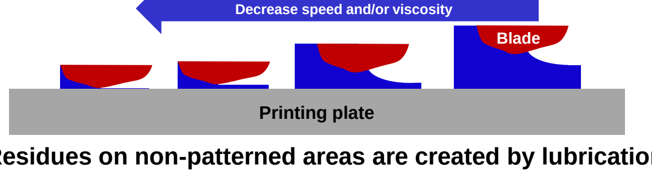
Wiping on Non-patterned Areas



Dimensionless speed: $U^* = \frac{\eta_0 U}{E'R}$

For our system, Ca=1E8×U*



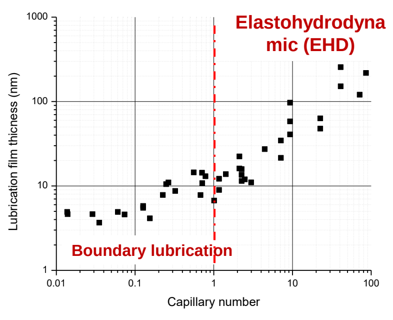


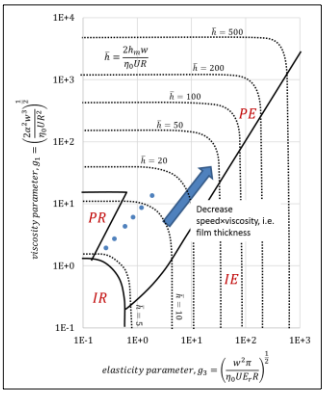
Residues on non-patterned areas are created by lubrication films between the blade and printing plate.

Lubrication Films in Gravure

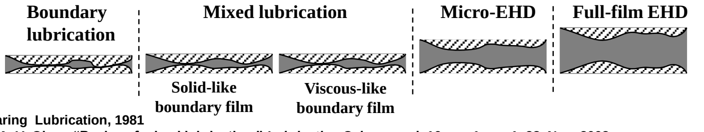
Film thickness[1] : $h \propto U\eta^{0.67}$

Lubrication regimes[3]:



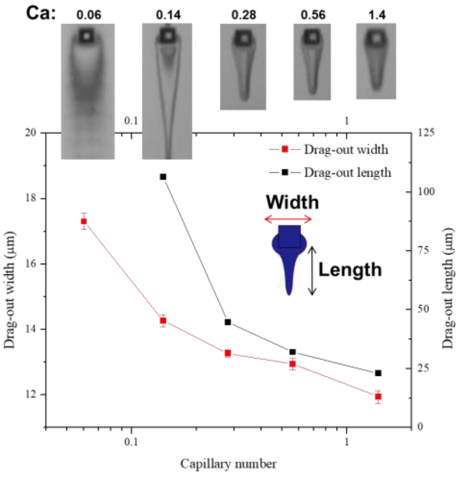


Regions of EHD lubrication films[2] :

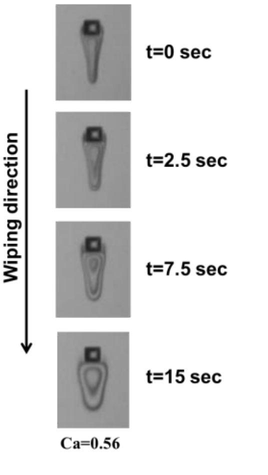


[1]Dowson, Ball Bearing Lubrication, 1981
[2]H. A. Spikes and A. V. Olver, "Basics of mixed lubrication," *Lubrication Science*, vol. 16, no. 1, pp. 1–28, Nov. 2003.
[3]Johnson, K. L. , "Regimes of elastohydrodynamic lubrication", *Journal of Mechanical Engineering Science 12*(1), 9–16, 1970.

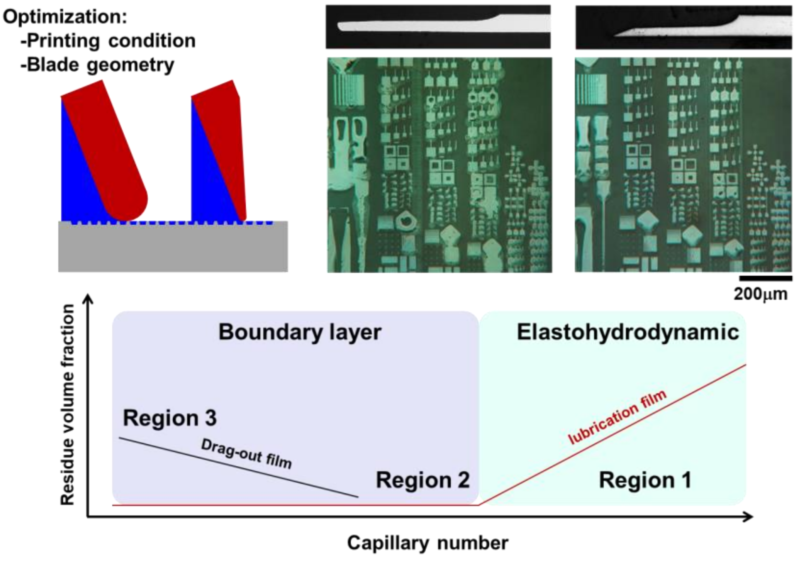
Characteristic of Drag-out Tails



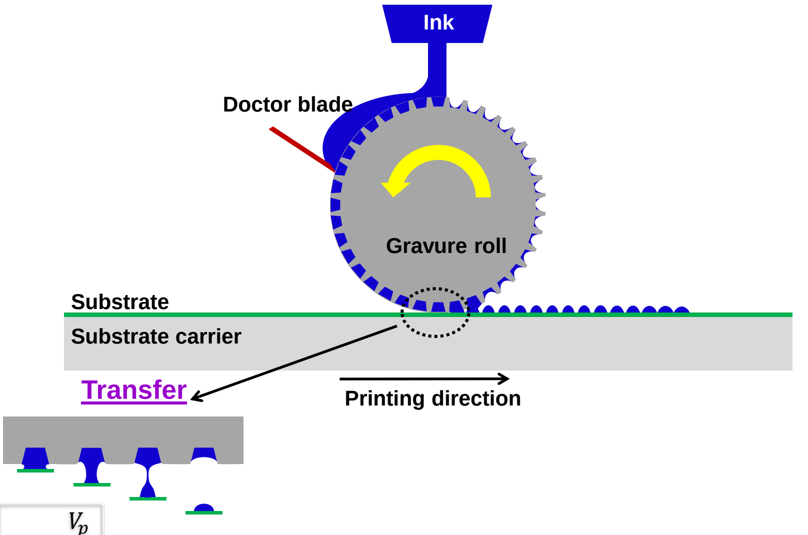
After released from doctor blade



Perfect Wiping

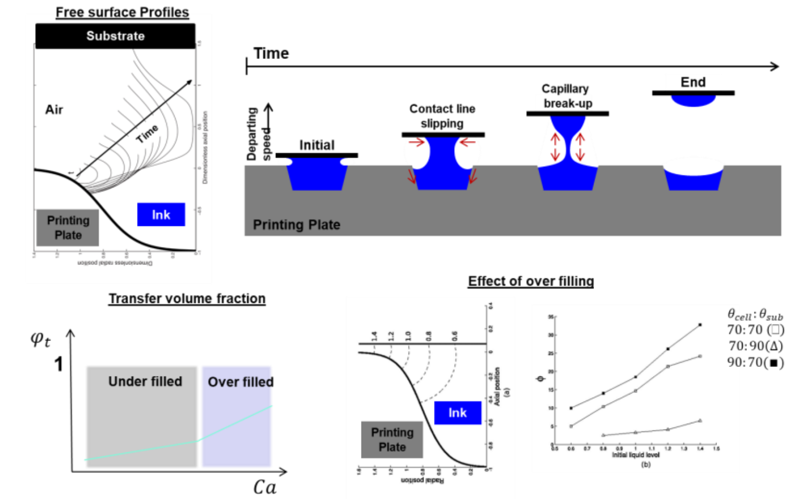


Transferring Process



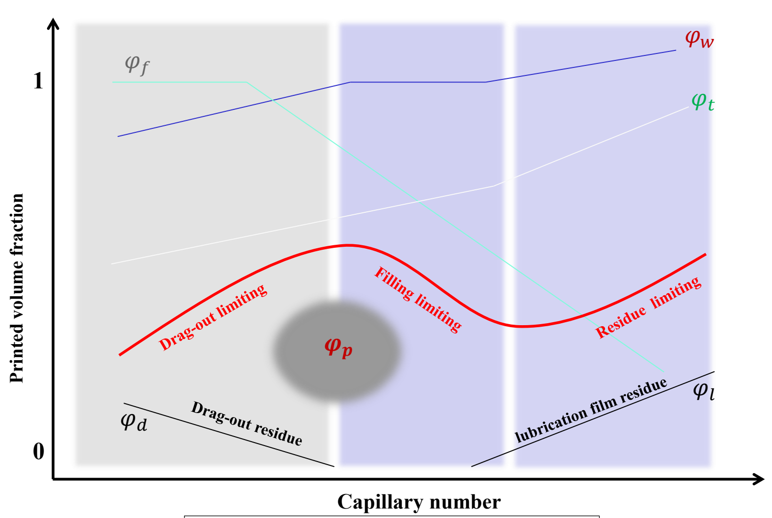
$$\varphi_t = \frac{V_p}{V_r}$$

Transfer Mechanism



Shawn Dodds, Marcio da Silveira Carvalho, and Satish Kumar *Physics of Fluids* 21, no. 9 (2009): 092103

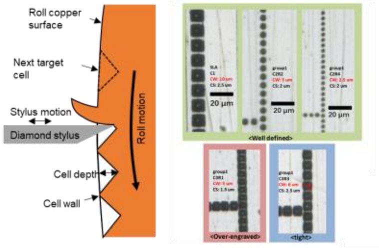
Characteristic of Gravure Printing



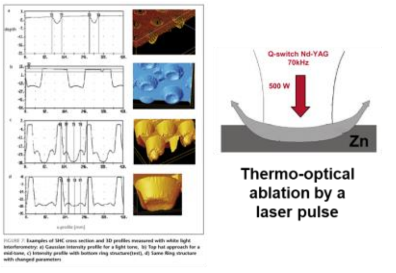
Printed volume fraction: $\varphi_p = \varphi_f \varphi_w \varphi_t$

Current Roll Engraving Technology

Electromechanical (EM)

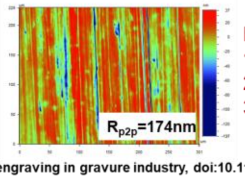


Direct Laser (DLS)*



Thermo-optical ablation by a laser pulse

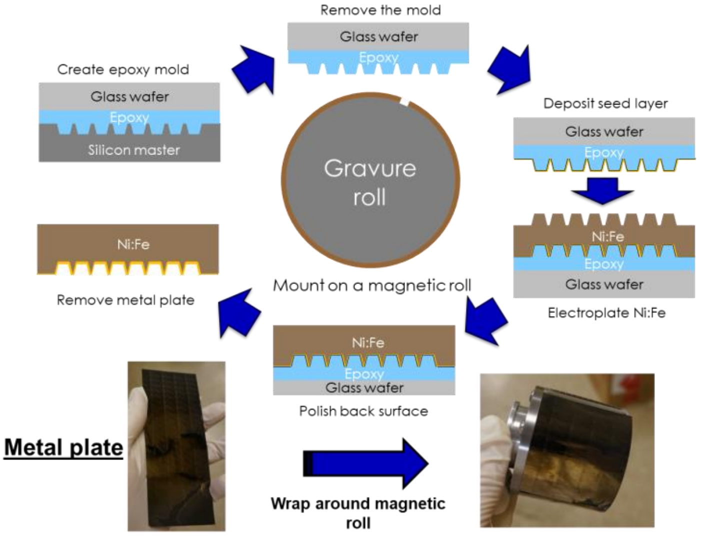
Surface finishing



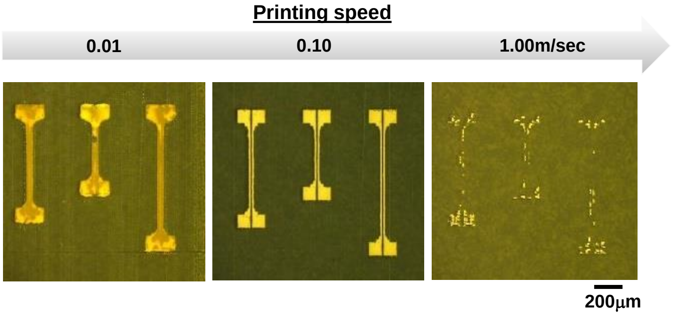
Limitations:
1) Minimum cell size
2) Incorporate various cell sizes closely
3) Surface roughness

*Hennig, G (2005). Laser engraving in gravure industry, doi:10.1117/12.660938

High-Resolution Roll Fabrication



Printed Volume Fraction



<2μm Printed Channel