PY5020: Nanoscience

INKJET Printing

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Overview

- Microfluidics

- Continuous flow
  Plateau instability

- Drop on demand
  Thermal
  Piezoelectric

- Ink & Wetting effects

- Applications of inkjet printing
  Organic electronics
  Layered materials

- Aerosol Jet

Siphon recorder (1858)

First modern inkjet (1952)
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

![Diagram showing the difference between a solid and a fluid](solid-vs-fluid.png)
Fluids have viscosity

\[ \tau = \mu \frac{du}{dy} \]

where

\( \tau \) is the shearing stress
\( \mu \) is the absolute dynamic viscosity
\( \frac{du}{dy} \) is the velocity gradient

In addition:

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

Thermal effects
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**
\( \Delta P = 3 \text{ bar}, R = 5 \text{ cm} \)
\( \mu = 0.01 \text{ poise}, L = 10 \text{ m} \)
\( V = 73 \text{ m/s} \)

**Washing machine**
\( \Delta P = 3 \text{ bar}, R = 1 \text{ cm} \)
\( \mu = 0.01 \text{ poise}, L = 5 \text{ m} \)
\( V = 0.2 \text{ m/s} \)

**Ink-jet printer**
\( \Delta P = 3 \text{ bar}, R = 100 \mu \text{m} \)
\( \mu = 0.01 \text{ poise}, L = 5 \text{ cm} \)
\( V = 20 \mu \text{m/s} \)
Which leads to Reynold’s 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
- \( \rho \) is the fluid density
- \( V \) is the fluid velocity
- \( D \) is the pipe diameter
- \( \mu \) 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”
Reynold’s number and scaling

<table>
<thead>
<tr>
<th>Household pipes</th>
<th>Washing machine</th>
<th>Ink-jet printer</th>
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<tbody>
<tr>
<td>$\Delta P=3$ bar, $R=5$ cm</td>
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Water density $= 10^3$ kg.m$^3$
Viscosity $= 10^{-3}$ kg.s$^{-1}$.m$^{-1}$

Re=$3.65 \times 10^6$  
Re=2000  
Re=$2 \times 10^{-4}$

- 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!
Reynold’s number and laminar flow

Reference: Van Dyke, *Album of Fluid Motion*
Continuous flow ink jet (CIJ) printing
Plateau instability

- Phenakistiscop (to look at a lie)
- First moving picture
- Laws that describe soap bubbles
- Behaviour of a column of fluid confined by surface tension (1856)

Joseph Plateau
1801-1883
Belgian
Rayleigh-Plateau instability

- Initially a cylindrical stream
- Small perturbations form *(Varicose perturbations)*
- Young Laplace:
  \[ \Delta p = \frac{2\gamma}{R}. \]
- Pinched regions rupture
- Drop formation at critical wavelength for stream
- Mathematically described by Rayleigh in 1874

Parallel with spacetime – “black string”

Coating of optical fibres

Dimensional analysis

\[ L_{\text{crit}} = f(\rho, R, U_{\text{jet}}, \gamma) \]

- \( \rho \): density
- \( R \): column radius
- \( U_{\text{jet}} \): jet stream velocity
- \( \gamma \): surface tension

\[
\frac{L_{\text{crit}}}{R} \sim U R^a \rho^b \gamma^c = U [L]^a \left[ \frac{M}{L^3} \right]^b \left[ \frac{M}{T^2} \right]^c
\]

Leading to a solution:

\[
\frac{L_{\text{crit}}}{R} \sim U \left[ \frac{\rho R}{\gamma} \right]^{1/2} \quad \text{and} \quad T_{\text{crit}} = \left( \frac{\rho R^3}{\gamma} \right)^{1/2}
\]

- An increase in velocity or stream radius can reduce the instability
- Other results which come from an analytical solution

\[
f_{\text{droplet}} \sim \lambda U_{\text{jet}}
\]

\[
R_{\text{drop}} \approx 2.1 R_{\text{col}}
\]
Continuous flow ink-jet

- Rayleigh-plateau instability drop source
- Design-specific destabilization frequency
- Statically charged drops
- Electrostatically deflected stream of drops
Continuous flow ink-jet

Droplet formation

1. Emission of cylindrical plug from orifice
2. Varicosity
3. Sectioning into thinner and thicker zones
4. Ligaments break
5. Electrical connection to print head cut

Droplet sizes and rates

- Orifice diameter typically 50 μm to 80 μm
- Droplet diameter roughly exceeds orifice diameter by factor of two
- Droplet sizes below 150 μm common
- Volumes between 4 fl and 1 pl
- Droplet frequencies in order of 100 kHz
- Special devices up to 1 MHz

Satellite droplets

- Frequently formed
- High $q / m$ ratio
- Large deflection
- Erroneous droplets
Short history of CIJ

1951: Elmqvist from Siemens files first patent for device based on Rayleigh principle

- “Measuring instrument of the recording type”, U.S. Patent 2566443 (1951)
- Mingograph: first ink-jet based writer for recording analogue voltage signals

1960s: Sweet (Stanford University)
- Distinct pressure wave patterns
- Applied to orifice of liquid column
- Jet breaks up into equally spaced droplets of same volume

1970s: IBM licenses continuous ink-jet technology (cIJ)
- Dedicated charging of droplets
- Recirculation by deflection in transversal electrical field

1976: IBM 4640 (Word-Processing Hardcopy-Output application)
Contemporary CIJ applications
Drop on Demand ink jet printing
Drop on demand principle

**Fig. 8.3.** Impulse technology

**Fig. 8.4.** Droplet formation in impulse-type devices. The 50-μm droplets are issued from an orifice of the same diameter at a frequency of 2 kHz.
Mechanisms for DoD droplet formation

- **Thermal**
  - Commercial systems
  - Limited applicability for functional inks
- **Piezo-electric**
  - Research systems
  - Wide ink applicability
- **Electrostatic (Electrohydrodynamic)**
  - Exploits scaling properties of Electrostatics
  - Conductive fluid required
- **Acoustic**
  - Reduced clogging
  - Small volume drops (65 fl reported)
Thermal drop formation

- Heating (some μs)
  - Overheated ink
  - At 300°C: nucleation of bubble

- Expansion
  - Ejection of ink
  - Parallel to bubble expansion
  - Bubble pressure (empirical)

\[ p[T(t)] = (p_{nuc} - p_{vap}) \exp \left( \frac{t}{\tau} \right)^{1/2} + p_{vap} \]

- Droplet formation
  - Collapsing vapor bubble
  - Retraction of bulk ink
  - Refilling of cavity (80-200 μs)
    - Speed-critical step
Thermal bubble generation profile
Piezoelectric drop formation

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

Tailorable!!!!
Short history of DOD

1970s: On-Demand (DoD) Technology
Pressure generated by voltage pulse applied to piezo element
Siemens (PT-80 serial character printer, 1977)
Lots of clogging poor pulse control

1979: Cannon develops bubble jet (BJ) technology
HP independently develops a thermal bubble technique (thermal Ink-Jet)

1984: Thinkjet by Hewlett Packard
First commercially successful low-lost printer based on BJ-principle
Disposable cartridges eliminate reliability/clogging problems

1990s: low-cost colour ink-jet printer become standard equipment in home and office solutions

2000s: Tailorable drop dynamics and semiconducting inks introduce ink jet printing as a device fabrication method (Xerox, Samsung, Philips)
DoD Ink Formulation

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

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

Where
- \( \rho \) is the fluid density
- \( V \) is the fluid velocity
- \( D \) is the pipe diameter
- \( \gamma \) is the surface tension

The Ohnesorge number is the ratio of the Reynolds and Weber 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
Pattern Formation

- Patterns of dots
- Dot spacing

Wetting
\[ \gamma \cos(\theta_{eq}) = \gamma_{SL} - \gamma_{LG} \]

Drying effects

Substrate choice

\[ \gamma_{\text{ink}} < \text{Substrate surface energy} \]
- Coating
- Functionalizing
Coffee ring effect

• Convective flow
  Increased evaporation at edge

• Mangaroni effect
  High surface tension pulls volume more strongly
  Legs in a glass of wine

• High temp gelation inks
• Mixed solvents tension/evaporation
• Substrate optimization
Building a transistor

- Multiple layers deposition
- Insulating, semiconducting, conducting inks (2000 Nobel prize)
- Sintering
- Low resolution
- Serial process

(a) pentacene; (b) sexithiophene (α-6T); (c) poly(3-hexylthiophene) (P3HT); (d) poly(thiénylenevinylene) (PTV); (e) poly(9,9′-dioctylfluorene-co-bithiophene) (F8T2).

Self-aligned printing

Ink jet printing ~ 10um linewidth

Ink-jet devices – operation speed limitation

1) First conductive pattern is printed
2) Surface energy of the pattern is lowered without changing the substrate
3) Second conductive pattern is printed on top of the first

Achieve sub micron feature separation

All-inkjet TFT devices

More surface energy effects

- Traditional patterning
- \( \mu \)-contact printing
- Surface curvature
- Plasma functionalization
Inkjet OLED

- Solubility of polymers and some oligomers
- High functionality of semiconducting inks
- Transport, Blocking, Emission layers
- Inkjet for multi-ink process
- Patterning for pixel control logic (all organic)
- AMOLED

**BLUE** - 4,4’-bis(2,2’-diphenylvinyl)-1,1’-spirobiphenyl (S-DPVBi)

**GREEN** - Tris-(8-hydroxyquinoline) aluminum (Alq3)

**RED** - 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM)
Inkjet Layered Materials

- Particles in ink
- Layered material
  - Shear exfoliation
  - Surfactants
- Material properties
  - Bandgap
  - Insulator
  - Photonic

Coleman Group

Nano Lett. 2014, 14, 3987–3992
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
Aerosol Jet
Next Lecture:

Transfer Printing

9am Tue 24th November