bubbles and droplets in microfluidics: formation, non-linear phenomena and applications.

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• microfluidics
  • simple fluids
  • droplets and bubbles
• formation of drops and bubbles
  • flow-focusing
  • T-junction
• stable oscillations with long periods
• time-reversible non-linear dynamics
• applications
  • micromixing, portable assays
  • micro-particles and micro-capsules
  • diffraction gratings
microfluidics

- small dimensions (10 – 100 µm)
- small rates of flow (~ 1 µL/s)
laminar flow

- small Reynolds #
- large Peclet #
- large surface/volume

Whitesides (1999)
number of papers containing the term "microfluidics"

motivated by • interest

enabled by • technology
enabling technology – soft lithography and rapid prototyping

planar geometries
rapid prototyping

design ~ 1 hour
print out ~ 1 day
fab master ~ 3 hours ~ 2 days

make copies of the device ~ 2 hours each
interest and applications

- chemistry (kinetics, organic / inorganic synthesis)
- drug design (hts)
- biotechnology (genomics, proteomics …)
- material science
- physics – new flow phenomena
- biology (cell response)
- optics

Whitesides, Harvard

Quake, Caltech

Ismagilov, UChicago
microfluidics with drops
applications

- controlled emulsification
- droplet as a beaker
  - aqueous chemistry
  - biochemistry
  - organic chemistry
- processing / screening / kinetics
- material synthesis
microfluidics with drops

• how do you make drops in a controlled way?

• how do you guide them through networks?
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emulsification

Ca $>>$ 1

We $>>$ 1

Bo $>$ 1

instability

capillary number (Ca) = viscous / interfacial
Weber number (We) = inertial / interfacial
Bond number (Bo) = gravitational / interfacial
Rayleigh-Plateau instability

\[ u \sim \frac{\gamma}{\mu} \quad \text{viscous dynamics} \]
\[ u \sim (\frac{\gamma}{\rho l})^{1/2} \quad \text{inertial dynamics} \]

→ typical size \( \sim \frac{1}{\lambda} \)
→ typically broad size distribution
micro emulsification

- liquid/liquid & gas/liquid
- possible to obtain narrow size distributions
flow focusing
flow focusing

confined (planar) geometry

inlets:
- rate of flow of the liquid ($Q$)
- pressure app. to gas stream ($p$)
results

bubbles:
• size: 10 – 1000 µm
• standard deviation < 5 %
• volume fraction: 0 – 100 %
scaling

\[ V_b \propto \frac{p}{Q \mu} \]
\[ f \propto pQ \]

simultaneous, independent control of the size and volume fraction
questions

\[ V_b \propto \frac{p}{Q\mu} \quad \text{no dependence on surface tension} \]

\[ f \propto pQ \quad \text{Ca: } 10^{-3} \text{ to } 10^{-1} \]

• why doesn’t surface tension come into the equations?
• what is the mechanism of break-up?
break-up: evolution of the interface

recording and image analysis

100 μm, 3000 times slower
single break-up

“speed of collapse”

dw/dt = f(Q, \mu, p, \gamma)
speed of collapse

\[ \frac{d\omega}{dt} = f(Q, \mu, p, \gamma) = \]
Speed of collapse

- The speed depends only on the rate of flow of the continuous fluid.
- The evolution is much slower than the speed of a capillary wave.
- Collapse is not driven by surface tension.

\[
dw/dt = f(Q, \mu, p, \gamma) = \alpha Q
\]

'Interfacial' speeds:
- **Viscous regime**
  \[ u \sim \frac{\gamma}{\mu} \sim 10-100 \, \text{m/s} \]
- **Inertial regime**
  \[ u \sim \left(\frac{\gamma}{\rho l}\right)^{1/2} \sim 1-10 \, \text{m/s} \]
‘squeezing’

fixed (constant Q) inflow

displacement at a speed proportional to Q

restricted outflow

but, is the thread stable?

\[ \frac{dk}{dr} \]
confinement

**equilibrium** shape for a given volume enclosed by the gas-liquid interface
equilibrium

no dynamics here
equilibrium
dynamics
simulation

end of the orifice
end of the gas
Inlet channel

surface evolver

experiment

dynamics

equilibrium
quasi-stationary break-up

break-up follows through a series of equilibrium states
bubble growth rate

resistance to flow in the outlet channel: \( R \propto \mu \)

rate of inflating the bubble: \( Q_{\text{gas}} \propto \frac{p}{\mu} \)

volume of the bubble

\[
V_b \propto t_{\text{open}} Q_{\text{gas}}
\]

\[
V_b \propto \frac{1}{Q} \left( \frac{p}{\mu} \right) = \frac{p}{Q\mu}
\]

as observed
rate of flow controlled break-up

• quasi-stationary break-up
  • break-up governed by the evolution of pressure
  • strong effects of confinement
  • slow compared to relaxation rates
  • (new) mechanism specific to microgeometries and low Ca

• bubbles
  • both the size and the volume fraction can be controlled

• applications
  • formation of emulsions (*food, cosmetics, ultrasound contrast, artificial blood*)
  • formation of monodisperse droplets *lab-chip, micro-particles, micro-capsules, lattices*
T-junction
mechanism of break-up

shear vs interfacial forces

linear size $\sim \text{Ca}^{-1}$

not checked rigorously

FIG. 4. Predicted vs actual drop size at different water and oil/surfactant pressures. The predicted sizes were calculated using Eq. (1). Open symbols, predicted size; solid symbols, experimental.

Thorsen (2001)
mechanism of break-up

100-fold change in shear stress
no change in size
forces

- interfacial stresses (stabilizing)
- shear stresses (destabilizing)
  overestimate scaling as $\varepsilon^{-2}$
- pressure drop (destabilizing)
  scaling as $\varepsilon^{-n}$ with $n>2$
‘squeezing’ –
– rate of flow controlled break-up

- blocking the channel
  \[ t_{\text{block}} \propto 1/Q_{\text{in}} \]

- squeezing
  \[ t_{\text{squeeze}} \propto 1/Q_{\text{out}} \]

size \( \sim (t_{\text{block}} + t_{\text{squeeze}})Q_{\text{in}} \)

size \( \sim 1 + Q_{\text{in}}/Q_{\text{out}} \)
scaling

\[ \frac{L}{w} \sim 1 + \frac{Q_{in}}{Q_{out}} \]
T-junction: simulations

simulations confirm both the details of the dynamics of break-up and the scaling

runs over a wide range of values of Ca show three distinct regimes:

**squeezing** – **dripping** – **jetting**

with **squeezing** being a new break-up mode, specific to microgeometries

M. De Menech, P. Garstecki, F. Jousse, H. A. Stone, *in preparation*
• **quasi-stationary break-up**
  
  • break-up governed by
  
  the evolution of pressure
  
  • strong effects of confinement
  
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coupled flow-focusing oscillators

1. **the rate of collapse of the thread at each orifice**
   depends on what happens everywhere else

2. **the exchange of information (via pressure waves)**
   is much faster than the evolution of the thread
multi-orifice: operation

period-1
multi-orifice: operation

period-7
**multi-orifice: operation**

**period-29**
multi-orifice: period 29
multi-orifice: period 29 – analysis

160 kfps – 6.25 µs
multi-orifice

• separation of time-scales for
  • (slow) break-up, and
  • (fast) exchange of information
  + dissipative dynamics (low to mod Re)
    ⇒ effective isolation of the system
• applications – Apollonian packings?
engineering size distributions

![Diagram of apollonian packing]

- Probability distribution of sizes.
- Evolution of packing over time.
- Size distribution graph with peaks at specific sizes.
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plug flow

increased resistance to flow,
\[ \Delta p \propto u^{2/3} \]

Taylor Bretherton Wong
plug flow – decisions

- Simple fluid will split as \( q_1/q_2 = R_2/R_1 \)
- A bubble has to make a decision
- Once it enters a channel it changes (increases) its resistance

A dynamic system with feedback (or memory)
One Loop

Period-1  Period-2  Period-3  irregular

frequency of feeding
One Loop

time

\[ t_n \]

\[ t_{n-1} \]
reversibility

\[ \eta \Delta \vec{V} - \vec{\nabla} P = 0 \]

invariant under:  \( V \rightarrow -V, \ P \rightarrow -P \)
period 1 ↔ period 7
symmetric signals

period 1 → period 2 → period 1

AAAAA → BCBCBC → AAAAAAA
coding – decoding
reversible flows

isolated events of amplification embedded in linear, reversible dynamics of flow

→ probing the fine line between non-linearity and reversibility

→ potential for automated and robust processing of signals on chip (potentially useful in lab-on-chip applications)
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mixing

2D, steady, incompressible flow:

\[ u = \frac{\partial \psi}{\partial y}, \quad v = -\frac{\partial \psi}{\partial x}. \]

integrable, no chaotic advection

\[ \frac{dx}{dt} = \frac{\partial \psi}{\partial y}, \quad \frac{dy}{dt} = -\frac{\partial \psi}{\partial x}. \]

it is difficult to mix fluids in microchannels
mixing – solutions

two-dimensional, steady flows

can we achieve exponential folding in a planar device and steady-state input?

passive mixers

active mixers

difficult fabrication always ‘on’
moving parts external control / agitation

Stroock (2002)

Beebe (2001)

S. Quake

Okkels (2004)

Stroock (2002)

Beebe (2001)

S. Quake

Okkels (2004)
mixer
alternating flow
alternating flow
crossing streamlines
folding of the interface

\[ d_{\text{inter}} \sim w \left(2^{-\frac{L}{a}}\right) \]

\[ d_{\text{diff}} = (tD)^{1/2} \]

\[ \frac{L}{a} = (2 \ln 2)^{-1} (\ln Pe - \ln (L/w)) \]

\[ Pe = \frac{Q}{Dw} = 10^5 \text{ for } Q = 1 \mu L/s, \ D = 10^{-6} \text{ cm}^2/\text{s and } w = 100 \mu m \]

number of chambers to mix the two liquid streams: \( \frac{L}{a} \sim 8 \)
mixing

\[ \text{Re} \in (10^{-2}, 10) \]

initial \( \text{Pe} \in (10^3, 10^5) \)

reduced to \( \text{Pe} < 100 \)
portability
vaxer

A portable platform
solution based micro assays
**vaxer**

A portable platform solution based micro assays
non-spherical particles
non-spherical particles
non-spherical particles
polyTPGDA: (a) microspheres, (b) a colloidal crystal of microspheres (c) rods, (d) disks, (e) ellipsoids, (f) spherical capsules, and (g) truncated microspheres. (h) agarose disks and (i) bismuth alloy ellipsoids.
interfacial polymerization

acid chloride in ‘oil’

diamine in ‘water’

→ semi-permeable microcapsules
In-situ interfacial polymerization

Diagram showing the setup for in-situ interfacial polymerization:
- (First inlet) diamine in water
- (Second inlet) hexadecane
- (Third inlet) acid chloride in hexadecane
- Glass tube
- Orifice
- Flow focusing
- Polymerization
- Nylon coated water droplets
- Quenching solution (dodecanol in hexadecane)
- Hexadecane with Span-80
micro-encapsulation
nylon capsules
nylon capsules
tunable diffraction gratings
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drops and bubbles in microfluidics

- control, reproducibility
- size, size distribution
- preparation of emulsions
- phenomena
- chemical kinetics, synthesis, materials
- analytical and portable systems