Engineering Dewetted Surfaces and Colloidal Deposits via a Droplet Deposition on a Solid Surface

Rajneesh Bhardwaj
Associate Professor
Department of Mechanical Engineering,
IIT Bombay, Mumbai

30th October 2017, IIT Bombay
Institute Award Lecture Series -2017

Image taken by M. Kumar
A simple lab (or office) experiment

A drop of coffee

Table top/Substrate

Dried deposit obtained on solid surface

Winerist.com

Deegan et al.
“Coffee-ring problem”

Is formation of ring universal to such systems?
If not, can we control the deposition of particles by leveraging complex and coupled transport phenomena inside the evaporating droplet?

First explained by Deegan et al., Nature, 1997
Motivation: Colloidal deposits

(a) Ring like pattern (Sommer et al, 2004)
(b) Central bump (Bhardwaj et al., 2009)
(c) Multiple ring patterns (Bhardwaj, unpublished)
(d) Fingering at wetting line (Bhardwaj, unpublished)
(e) Uniform deposition pattern (Sommer, 2004)
(f) Hexagonal cells (Truskett and Stebe, 2003)
A zoomed-in view of a part of the ring
Technical applications of the deposits

Bioassays, inkjet printing, particles sorting, colloidal crystals for photonics

Biomarkers
Blossey and Bosio, 2002


Park and Moon, Langmuir, 2006

Biosensors,
Trantum et al., 2014

Photonic colloidal crystals,
Jiang group, Univ. Florida
Dried droplets of blood

Biomarkers

Good health

Anemia

Hyperlipidemia

Brutin et al, 2011

Forensics (BPA)

Crimeforensics-scene.com
Motivation: Dewetted surfaces

- Self-cleaning, antifouling, anti-icing, low-drag surfaces

Dewetting

Scientific American, 2008
Dewetted surfaces in nature

Gao et al., 2007

Ensikat et al., 2011

Bush et al., 2008
Coupled physics

Impact

micro-/miliseconds

Evaporation

seconds/minutes

Time scales as diameter/velocity

1 mm droplet
1 m/s impact velocity
Spreading time ~ 1 ms

Blinking time of human eye ~ 200 ms
Classical transport of mass, momentum and heat

- Cooling of interface by latent heat of evaporation
- Marangoni stresses
- Laplace forces
- Dynamic wetting at contact line
- Laminar flow
- Convection
- Liquid vapor diffusion
- Heat conduction
### Methods

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Role of Marangoni convection

Particle moves radially outward

Particle returns to stagnation point

Increase in particles concentration at stagnation point

Uniform deposit formation: Influence of DLVO interactions

System: Water-glass-air-titania
Parameters: Diameter of particles = 25 nm, particles concentration = 2%
Volume of drops = 4-5 nL

Bhardwaj, Fang, Som, Attinger, Langmuir, 2010
Regime map

Radial flow driven by evaporation

Marangoni recirculation

Attractive DLVO force

\[
\frac{V_{\text{DLVO}^+}}{V_{\text{rad}}} \quad \frac{V_{\text{Ma}}}{V_{\text{rad}}}
\]

Uniform deposit

Central bump

Initial wetted diameter

Ring
Role of Substrate heating

Contact line pinning and Marangoni recirculation

Surface tension force

Hydrodynamic drag

van der waals force


Glass surface temperature (°C)
Marangoni velocity, VMa (m/s)
20 40 60 80 100

0.01
0.02
0.03
0.04
0.05
0.06

t1
t2
t3
t4

Radial position (µm)
Ring height (µm)
1200 1220 1240 1260 1280

1 mm

Ts = 27.5°C
Ts = 60°C
Ts = 90°C

(a)

Present measurements, c = 0.05 % (v/v)
Present measurements, c = 0.1 % (v/v)
Present measurements, c = 1 % (w/w)
Nguyen et al., 2013, c = 1 % (w/w)
Li et al., 2015, c = 0.25 % (v/v)

Thin ring with inner deposit

Ring

Inner deposit

Inner deposits

Initial wetted diameter

Initial wetted diameter

16/25
Self-sorting of particles

Marangoni flow

Stagnation region

Radial flow

Heated silicon

\[ \frac{D_{p1}}{D_{p2}}(t) \]

\[ D_{P1} \]

\[ D_{P2} \]

\[ D_{\text{range}} \]

\[ 1 \text{ mm} \]

\[ 0.4 \]

\[ 1 \text{ and } 3 \mu m \]

\[ 0.3 \]

\[ 1.1 \text{ and } 3 \mu m \]

\[ 0.2 \]

\[ \text{No ring with no self-sorting} \]

\[ 0.1 \]

\[ \text{Thin ring with self-sorting} \]

\[ 0.0 \]

\[ 20 \]

\[ 0.1 \text{ and } 3 \mu m \]

\[ 0.46 \text{ and } 3 \mu m \]

\[ \text{Substrate temperature, } T_s (^\circ C) \]

Patil, Bhardwaj, Sharma, to be submitted
Pure liquid droplet impact on microtextured surfaces

..and on microgrooved surfaces

$p = 0 \mu m$ (flat)  $p = 30 \mu m$  $p = 47 \mu m$  $p = 62 \mu m$  $p = 76 \mu m$

No bouncing  No bouncing  Complete bouncing  Bouncing with droplet breakup  Bouncing with droplet breakup

Initial condition

0.52 m/s  1 mm  0.82 m/s

No bouncing  No bouncing  Bouncing with droplet breakup  Bouncing with droplet breakup  No bouncing

Malla, Patil, Bhardwaj, Neild, Langmuir, 2017
Cassie to Wenzel Wetting Transition

Cassie state (complete non-penetration)

Partial wetting state (Partial-penetration)

Wenzel state (Complete-penetration)

Droplet

Pillared surface

Liquid-air interface

Liquid fills up between pillars

Depinning

Sagging

\[ \Delta P_{D} \]

\[ \Delta P_{H} \]

\[ \Delta P_{C} \]

\[ \theta_{adv} \]

\[ h \]

\[ h_{c} \]

\[ w \]

\[ p \]

Malla, Patil, Bhardwaj, Neild, Langmuir, 2017
Wetting characterization of Elephant ear (*Colocasia*) leaf

$\theta \sim 160^\circ$
Level-set based solver developed in Prof. Sharma group
Non-isothermal impact of a pure liquid droplet

Parameters: Isopropanol drop on fused silica, \(d_0 = 1.8\,\text{mm}, v_0 = 0.37\,\text{m/s},\)
Initial drop and substrate temperature = 25°C and 68°C, respectively

Acknowledgements

• PhD students
• Collaborator: Prof. Atul Sharma
• Funding: IRCC seed grant, DST Fast track
• IITB Central facilities: CEN, CRNTS
• Department facility: Profilometer, Infrared camera
• IRCC Award Committee
Questions, Comments?