School of Chemical and Process Engineering
FACULTY OF ENGINEERING

UNIVERSITY OF LEEDS

From Droplets to Particles – methods, insights and prediction

Andrew Bayly

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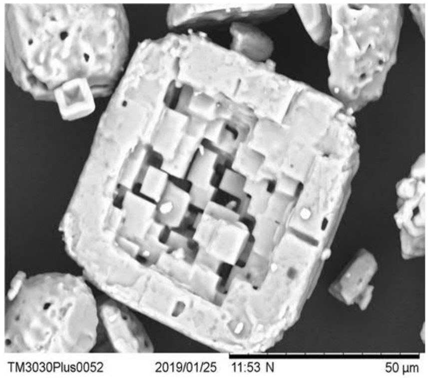


Formulation IV – Virtual Meeting June 2020

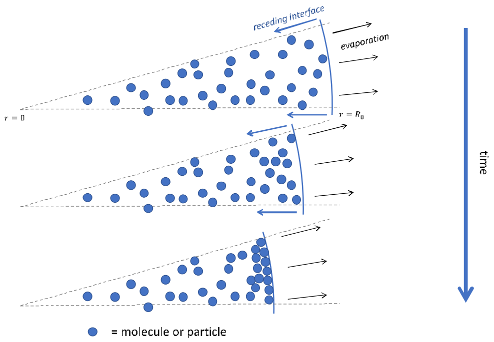
Who did the work!

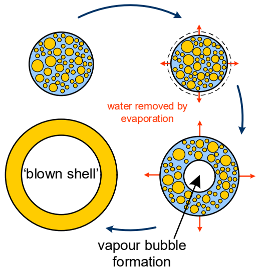
- Leeds: Wael Ebrahim, Karrar Al-Dirawi, Muzammil Ali, Arron Jones, Sam Lister
- Bristol: Jonathan Reid, Florence Gregson, Jim Walker, Dan Hardy, Justice Archer, Joshua Robinson, Patrick Royall
- Durham: Colin Bain, Lisong Yang, Jack Goodall

INSTITUTE OF
PARTICLE SCIENCE
& ENGINEERING

Factors Controlling Structure

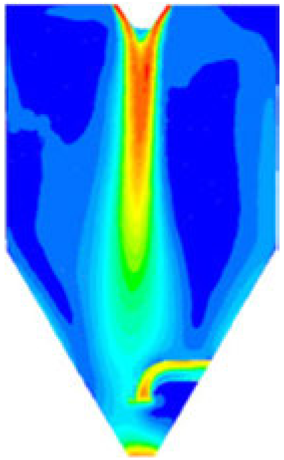
Single Droplet



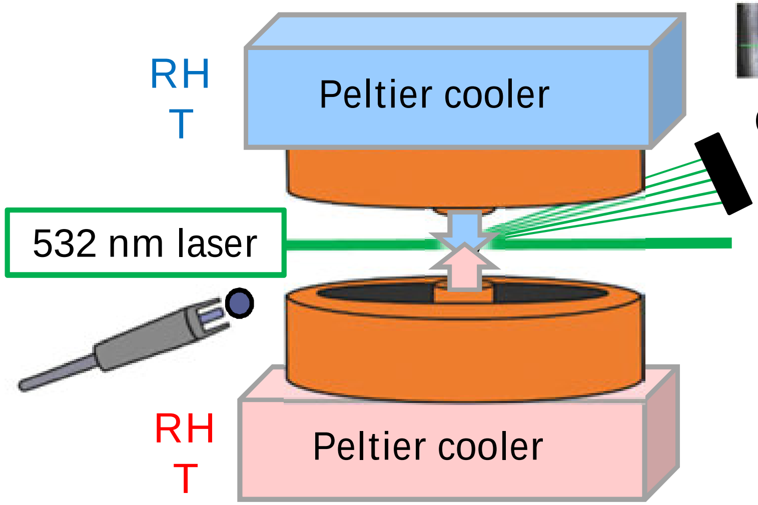


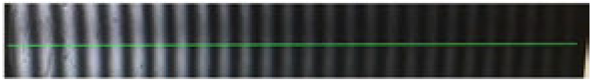
Droplet interaction

Process

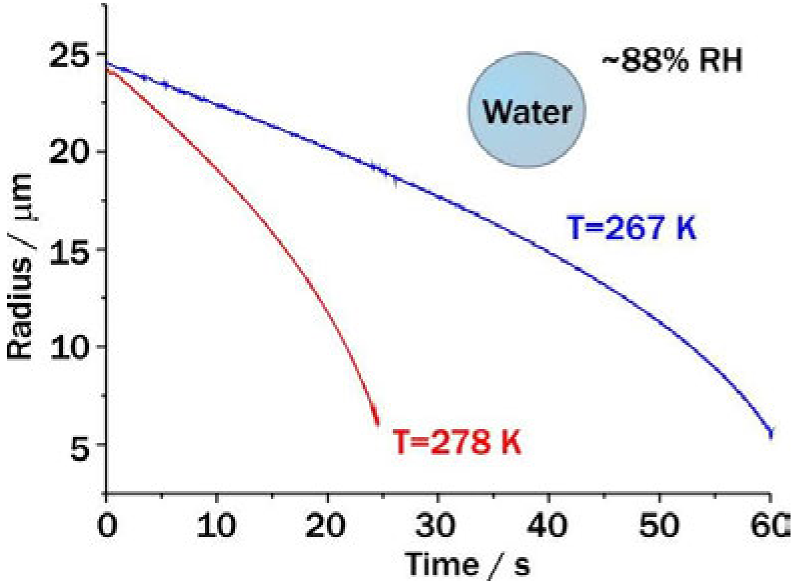


Studying Droplet Drying and Crystallisation





CCD collects elastic light scattering at 45°

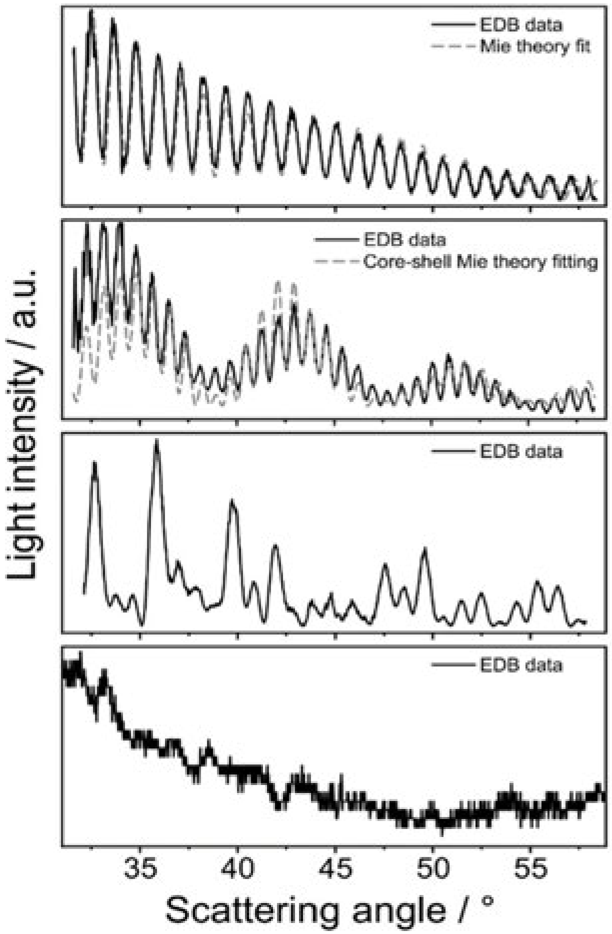


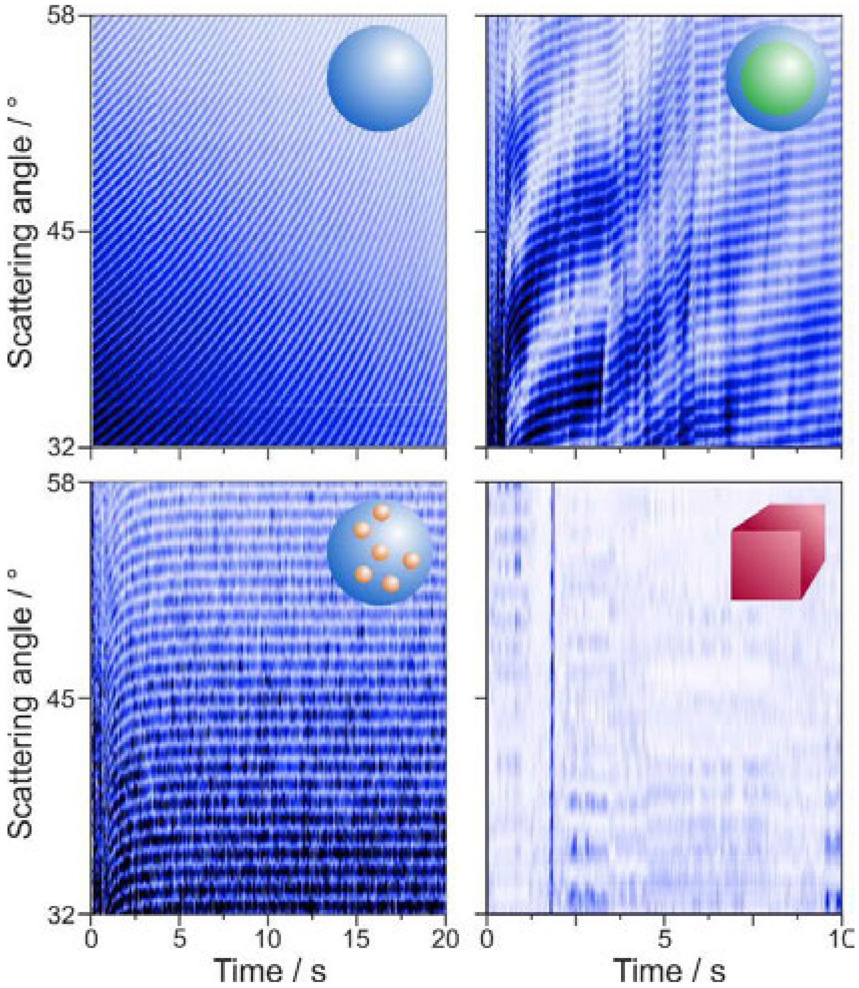
Electrodynamic Balance (EDB)

- 10 µL of sample, pL droplets.
- >4 µm radius.
- 10 ms time-resolution.
- -25 to >50 ^{o}C.
- 0 to >100 % RH.

Gregson, F. K. A., Robinson, J. F., Miles, R. E. H., Royall, C. P. & Reid, J. P. Drying Kinetics of Salt Solution Droplets: Water Evaporation Rates and Crystallization. J. Phys. Chem. B 123, 266–276 (2019).

Rapid Measurements of Evolving Morphology

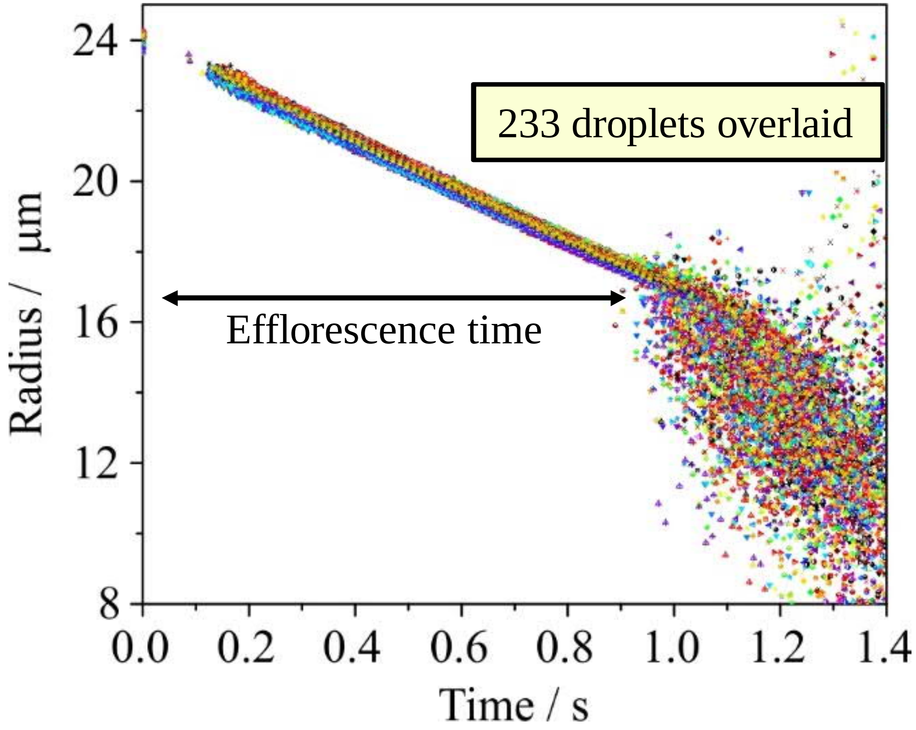


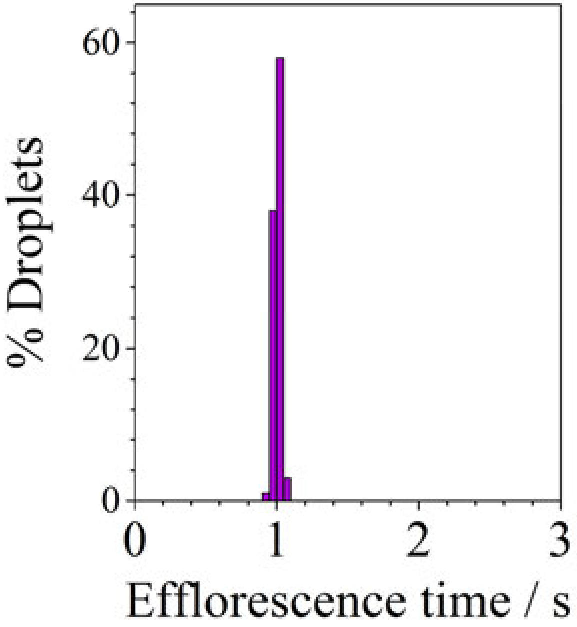


A.E. Haddrell, G. Rovelli, D. Lewis, T. Church and J.P. Reid, ‘Identifying time-dependent changes in the morphology of an individual aerosol particle from their light scattering patterns’, AS&T (2019) in press

NaCl - Abrupt Crystallisation, Well-Defined Supersaturation

NaCl evaporating into **dry** air (0% RH)
293 K





- Examination of concentration of solute and time at which crystallisation occurs shows high reproducibility.

Gregson, F. K. A., Robinson, J. F., Miles, R. E. H., Royall, C. P. & Reid, J. P. Drying Kinetics of Salt Solution Droplets: Water Evaporation Rates and Crystallization. J. Phys. Chem. B 123, 266–276 (2019).

Abrupt Crystallisation, Well-Defined Supersaturation

NaCl evaporating into **dry** air (0% RH)
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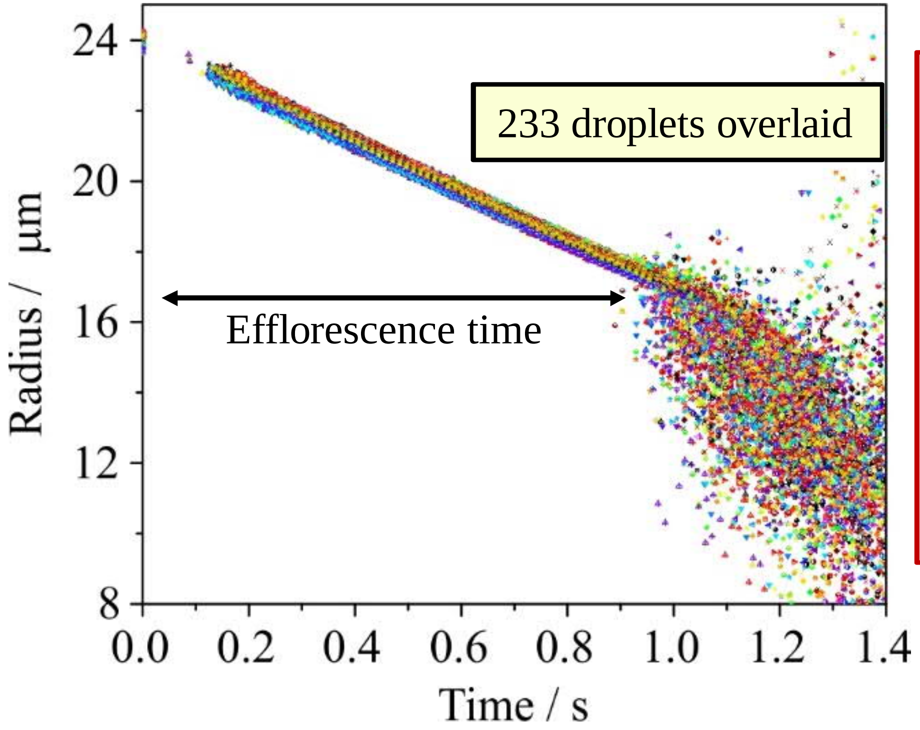

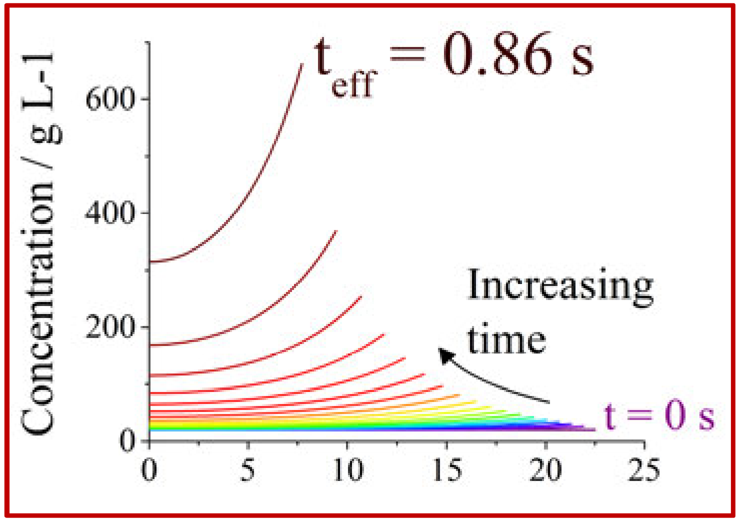

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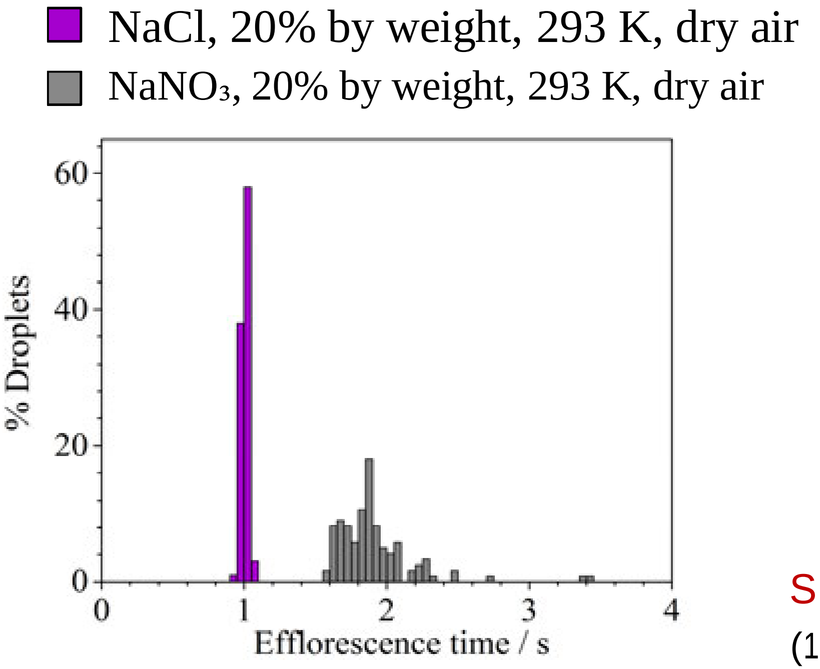
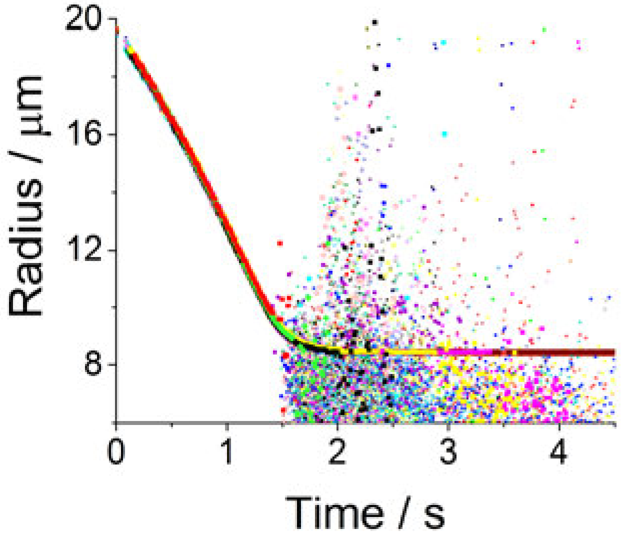
Different Salt - $NaNO_3$, Different Behaviour



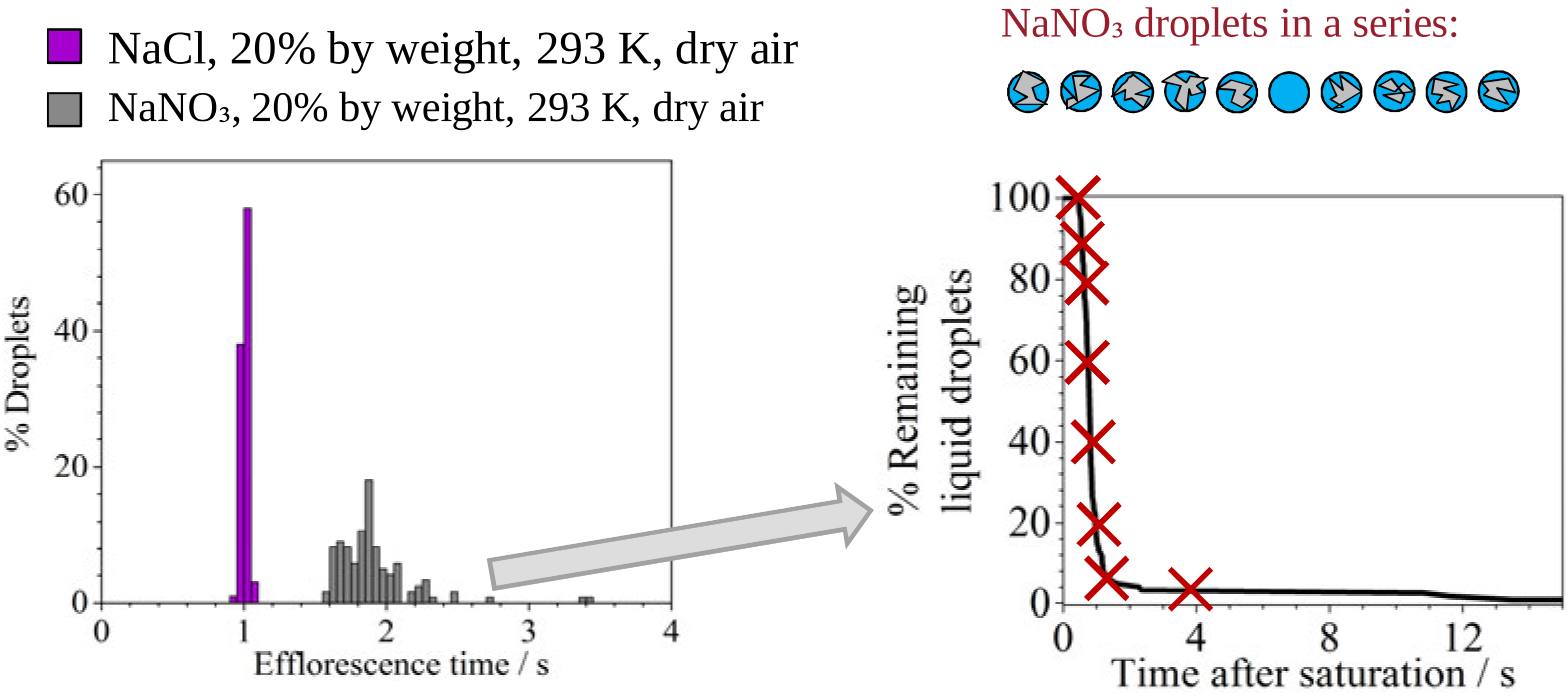


Sodium nitrate = highly variable

(133 droplets), 15% gas-phase moisture content, 293 K, Initial conc. 0.12 mass fraction

- Some droplets crystallise instantaneously while others reach a steady “equilibrium” size indefinitely.

Different Salt, Different Behaviour



🟪 NaCl, 20% by weight, 293 K, dry air

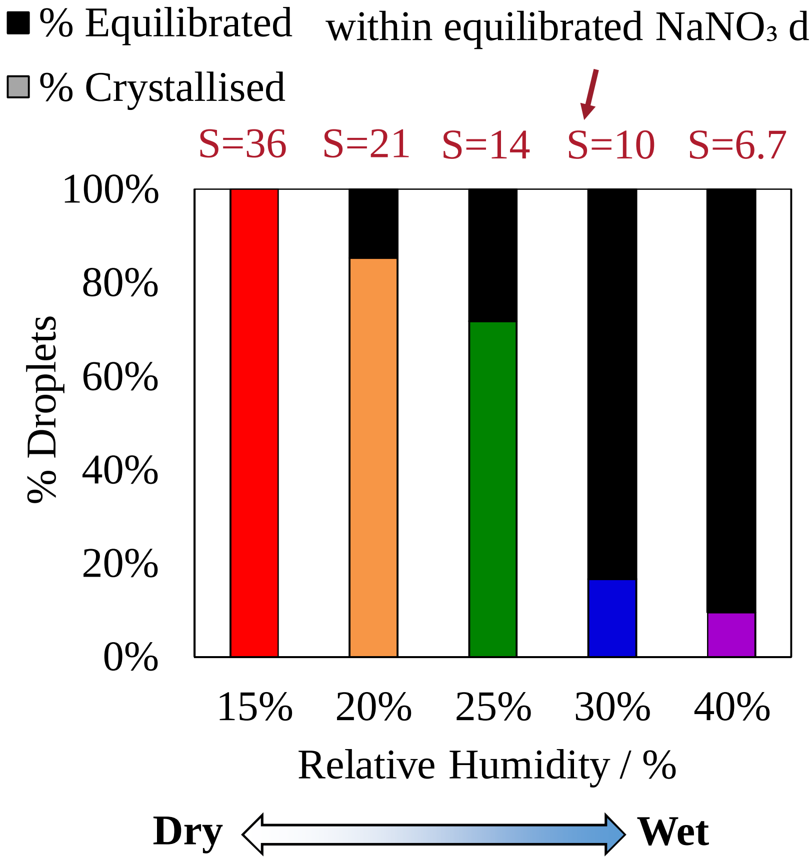
▨ $NaNO_3$, 20% by weight, 293 K, dry air

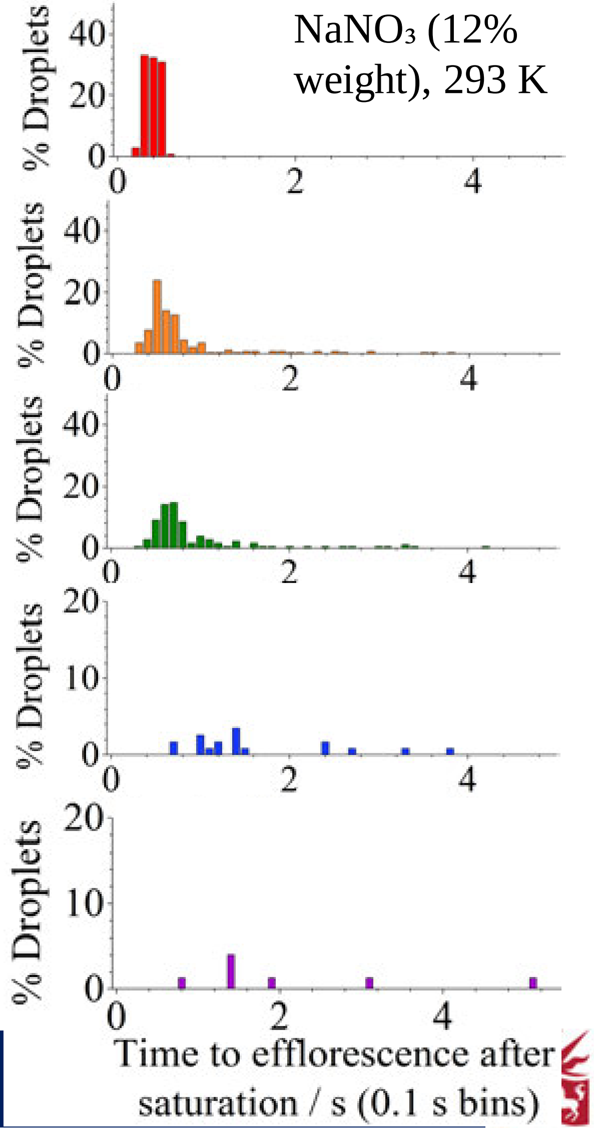
$NaNO_3$ droplets in a series:

- Some droplets crystallise instantaneously while others reach a steady “equilibrium” size indefinitely.

Dependence on Supersaturation/Drying RH

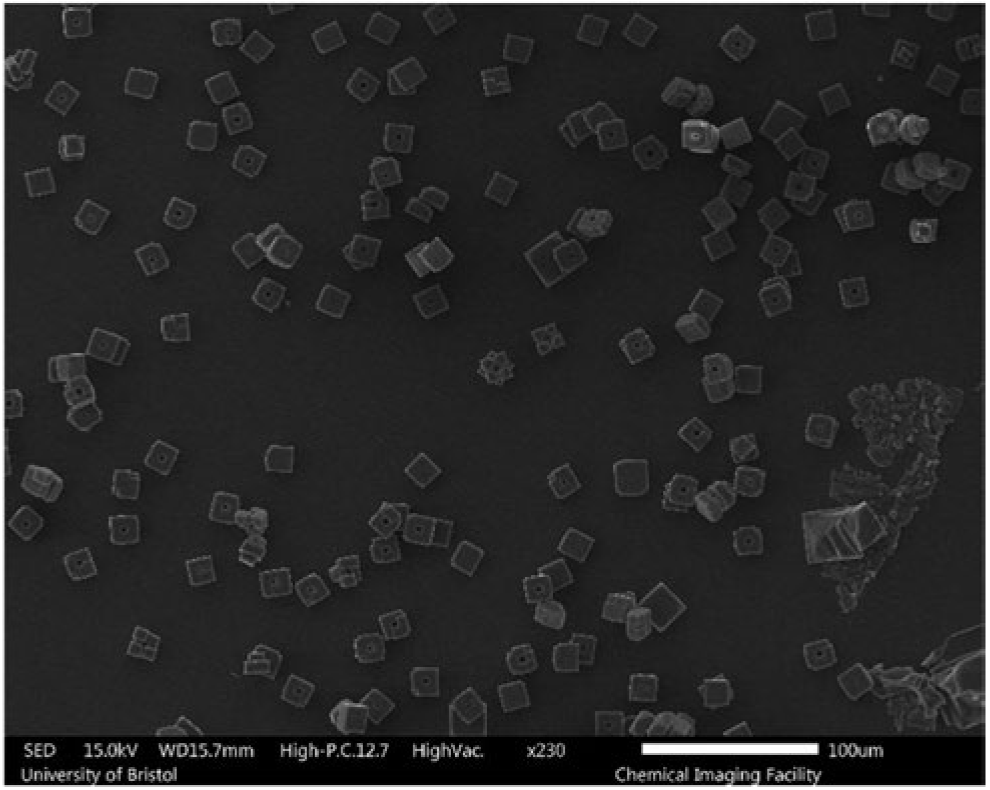
Level of solute supersaturation in molality within equilibrated $NaNO_3$ droplet at RH





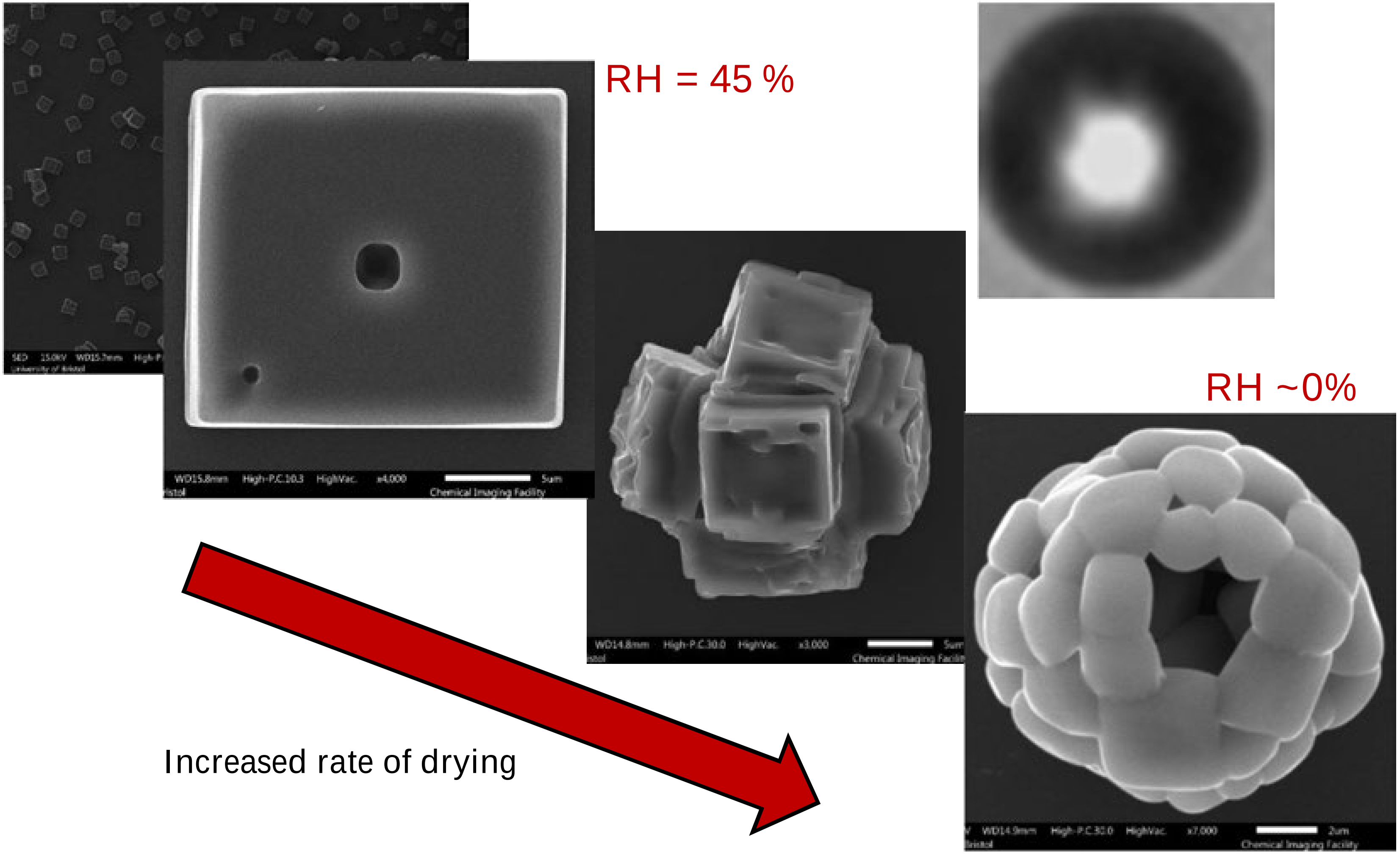
$NaNO_3$ (12% weight), 293 K

Morphologies in Falling Droplet Crystallisation



Add image of falling droplet

Morphologies in Falling Droplet Crystallisation

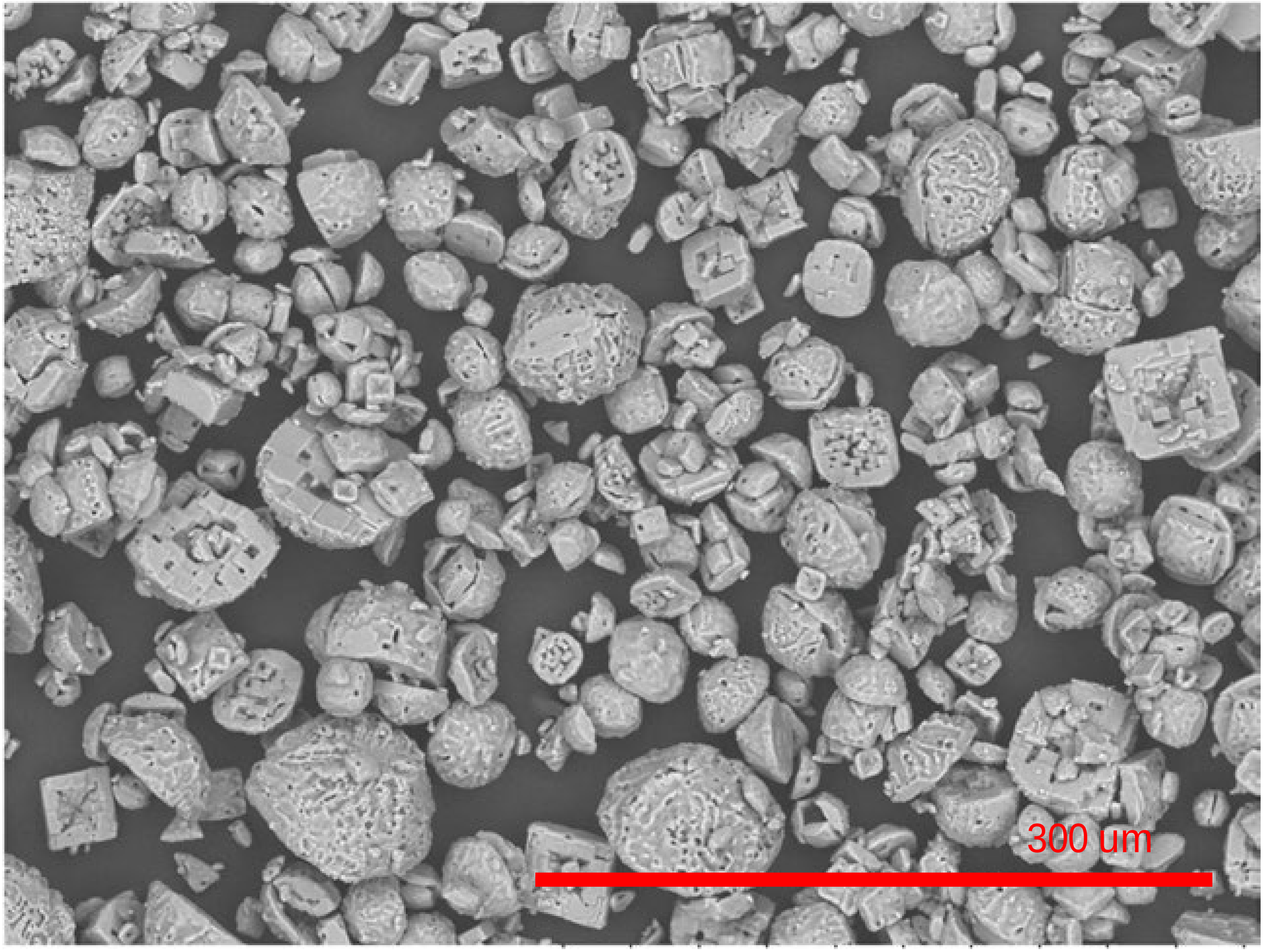


RH = 45 %

RH ~0%

Increased rate of drying

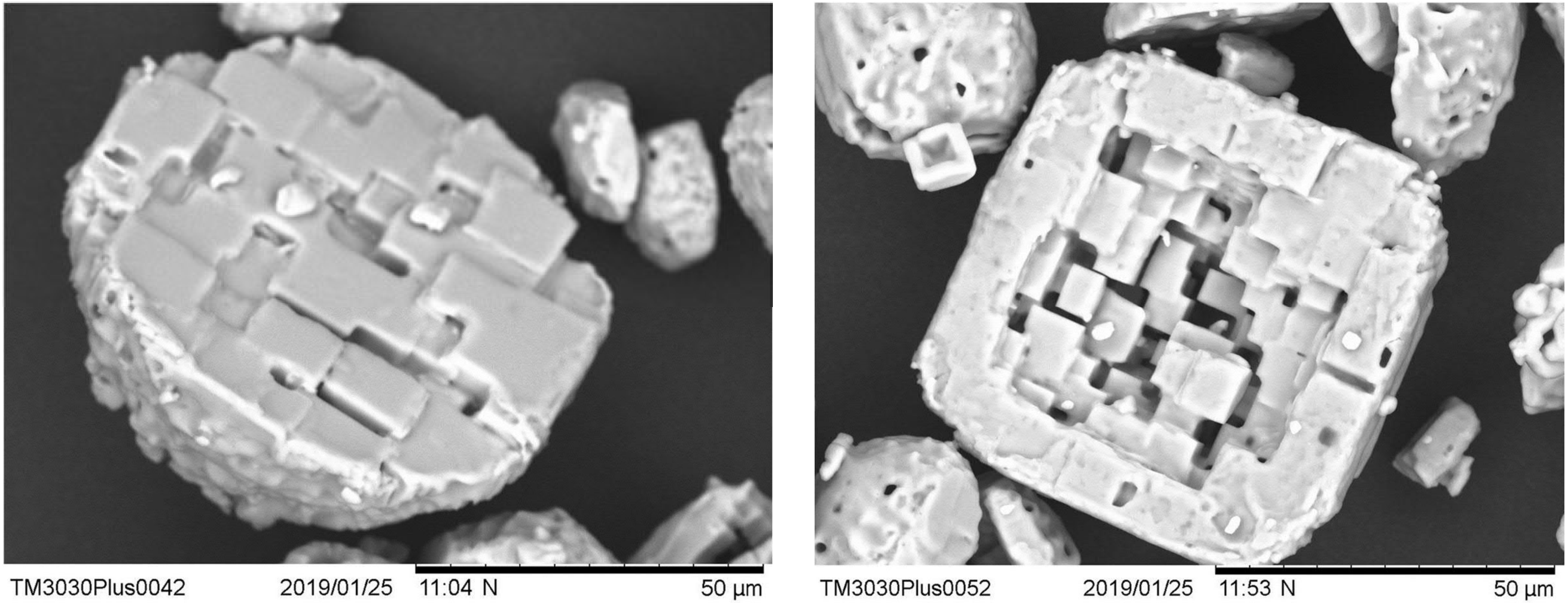
PARTICLE STRUCTURES FROM PILOT SCALE SPRAY DRYER



24% NaCl(aq.), 120 ºC

Procept Spray Dryer

Unusual structures



3-D hopper crystals

Manipulate Structure with Additives

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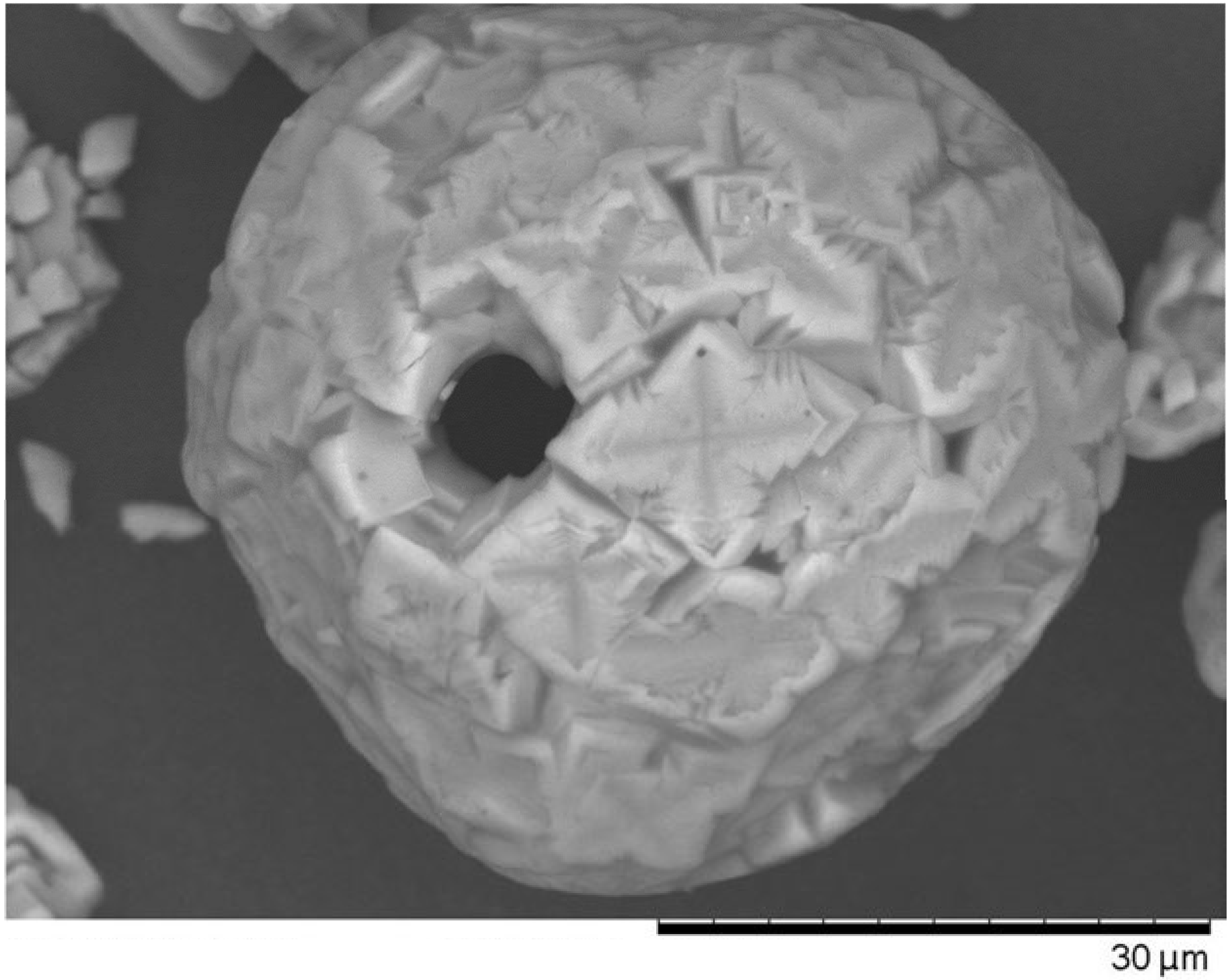


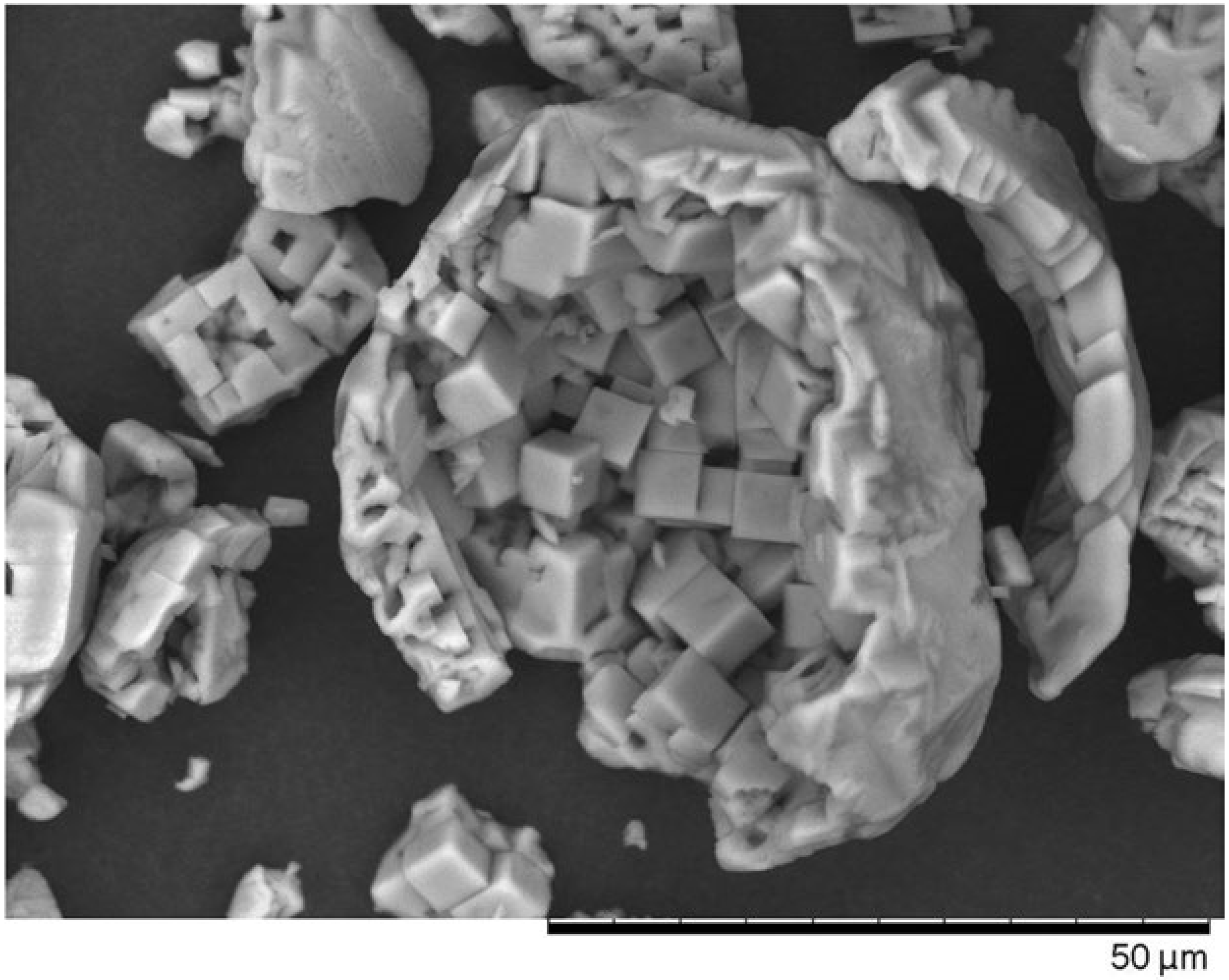
15% Soln NaCl

1% Maltodextrin

200 degC

Procept Dryer

Manipulate Structure with Additives



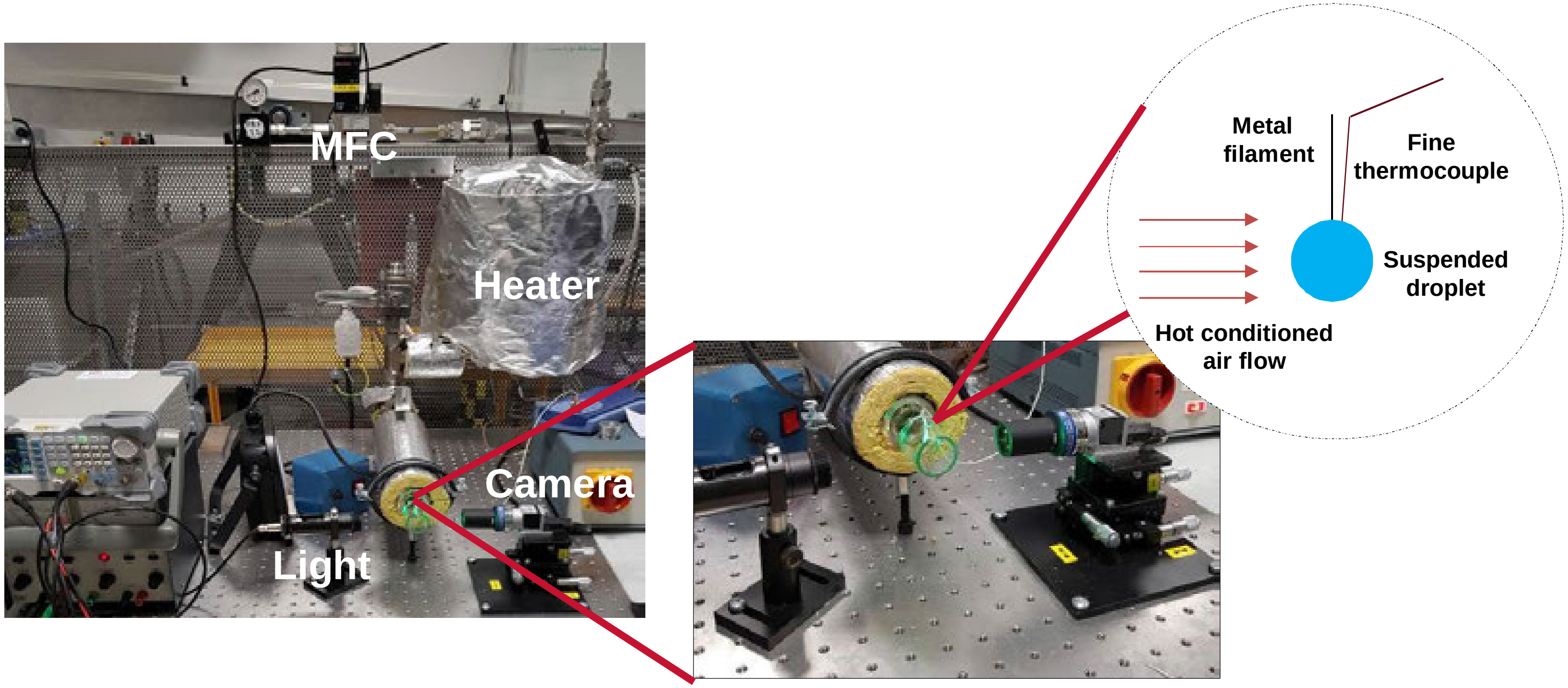
15% NaCl

1% Maltodextrin

200 degC

Procept Dryer

Filament Drying Rig



Nucleation and surface movement

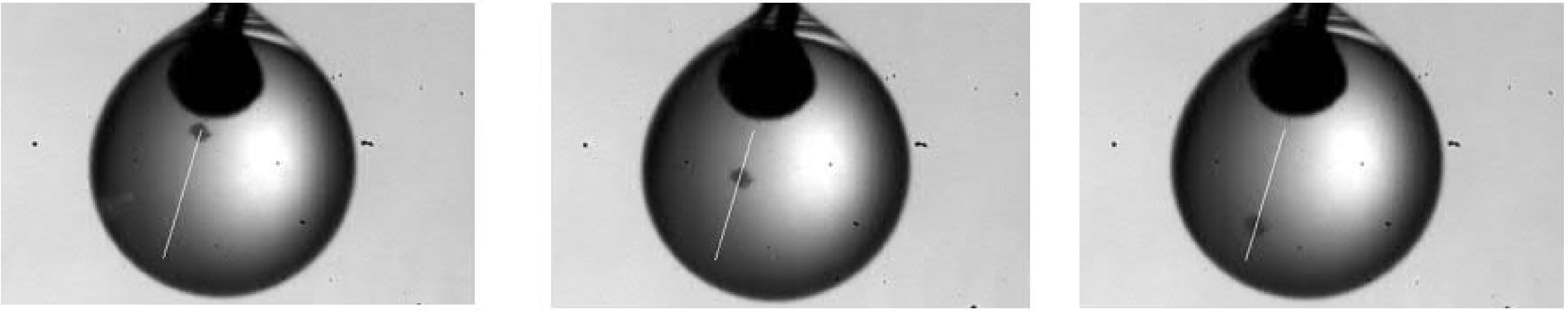


Figure 6.10: High Shutter Speed (2000fps) Images of SDD droplets of 15% NaCl Solution dried at 70°C

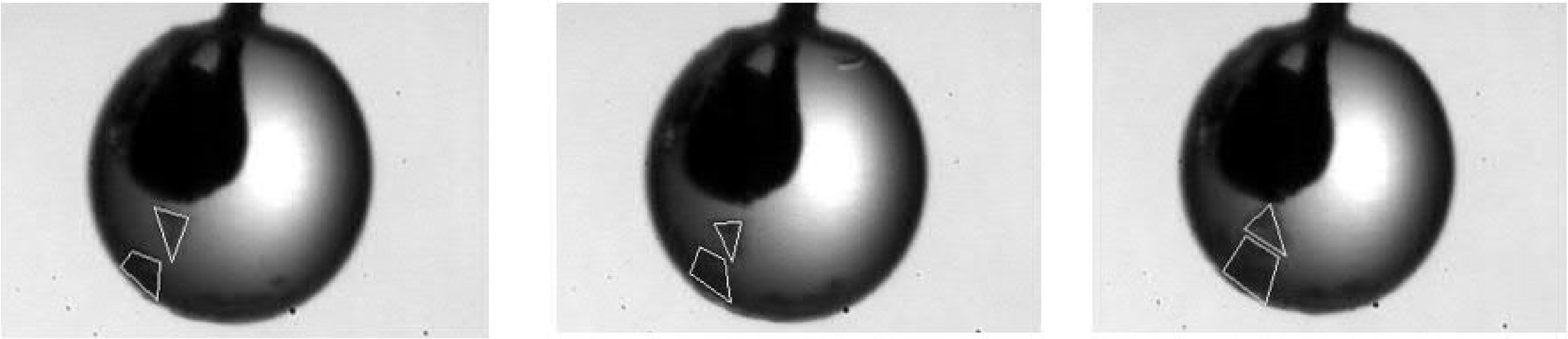
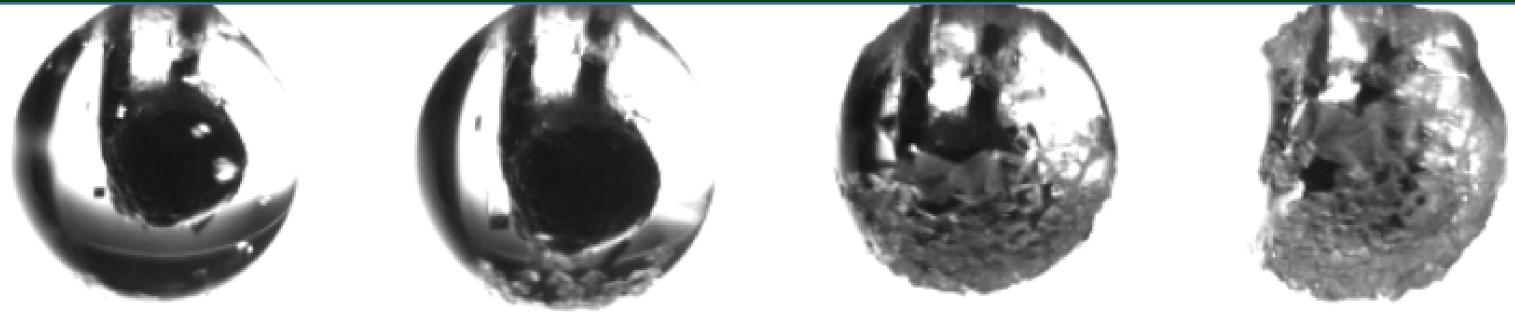


Figure 6.11: High Shutter Speed (2000fps) Images of SDD droplets of 24% NaCl Solution dried at 70°C

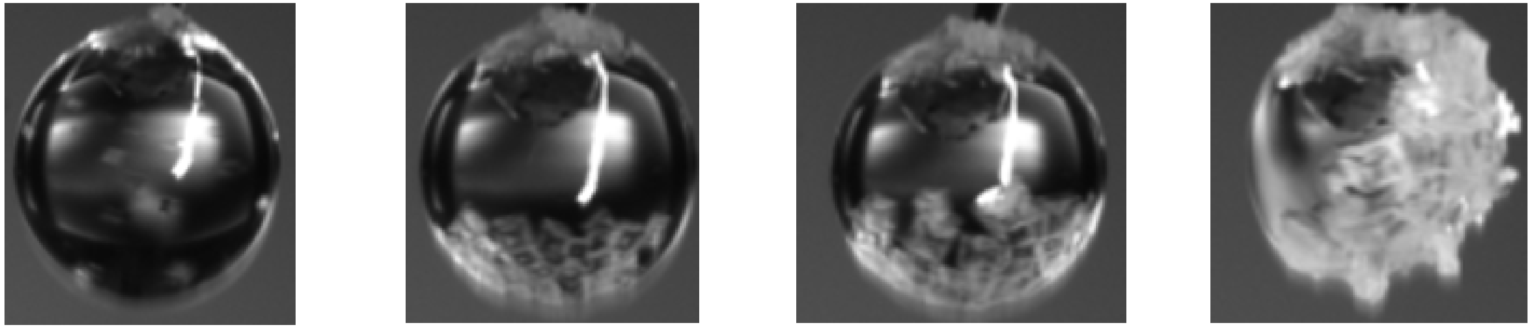
Hetrogeneous nucleation Gravity Capillary forces

Surface Growth



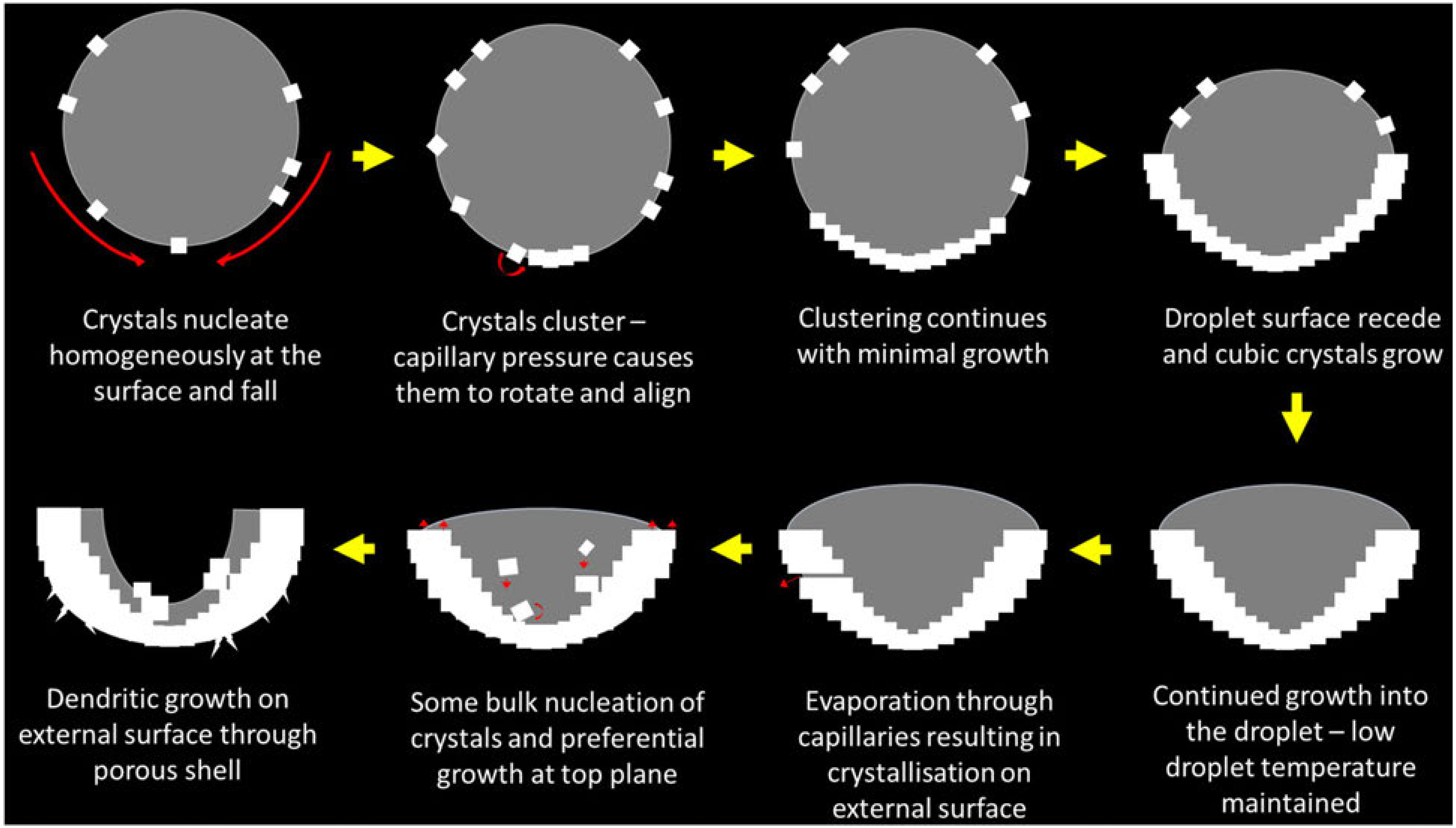
44s *54s* *78s* *100s*

Figure 6.8: Images of SDD droplets of 24% NaCl Solution dried at 70°C - imaged using non-polarised diffuse light. Images are labelled according to the time from start of drying.



74s *85s* *92s* *103s*

Figure 6.9: Images of SDD droplets of 15% NaCl Solution dried at 70°C - imaged using polarised diffuse light. Images are labelled according to the time from start of drying.



Crystals nucleate homogeneously at the surface and fall

Crystals cluster – capillary pressure causes them to rotate and align

Clustering continues with minimal growth

Droplet surface recede and cubic crystals grow

Continued growth into the droplet – low droplet temperature maintained

Evaporation through capillaries resulting in crystallisation on external surface

Some bulk nucleation of crystals and preferential growth at top plane

Dendritic growth on external surface through porous shell

Drying at High Temperatures

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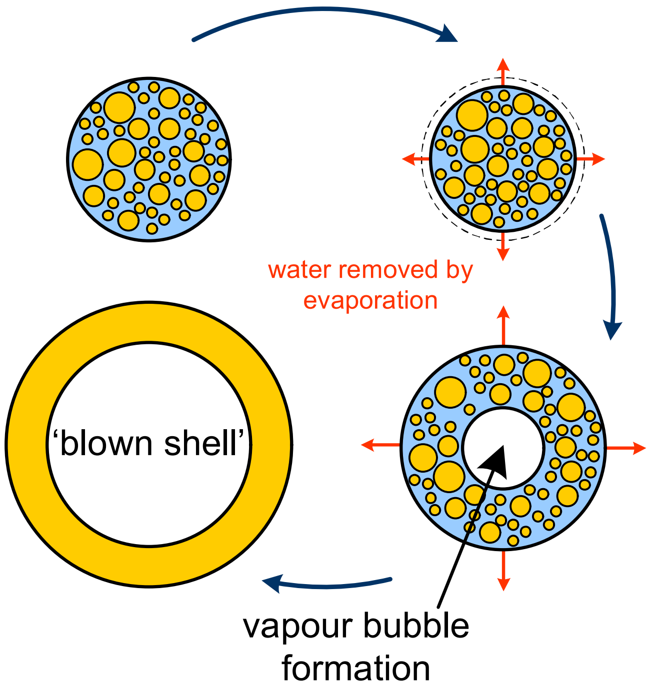

Bubble nucleation leads to mechanical deformation, puffing, and very significant changes in physical and functional properties

Droplet Drying History

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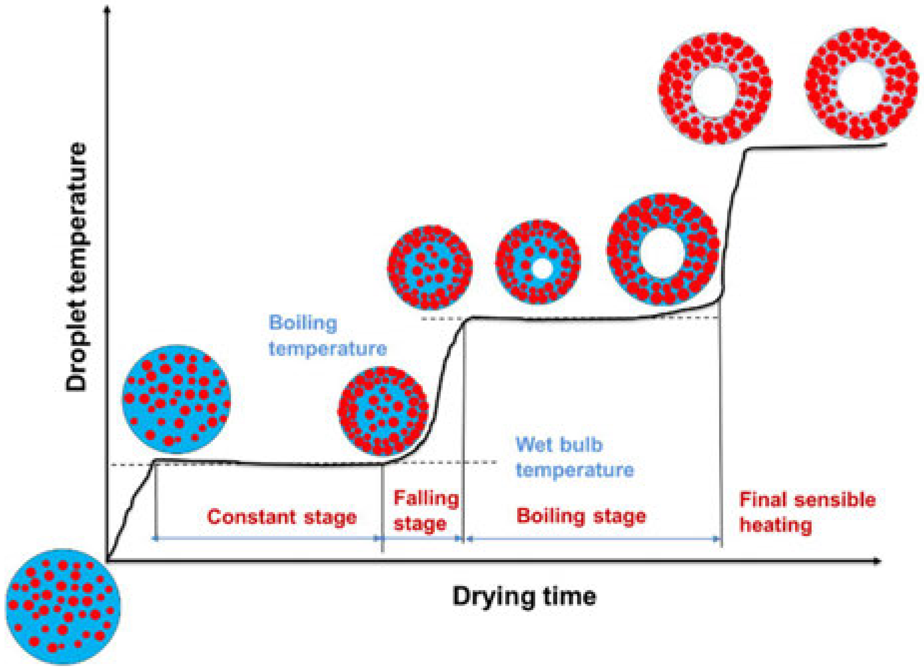
Drying kinetics

Structural evolution



The temperature history and morphological changes of a droplet in a spray dryer

Single Drop Drying Example

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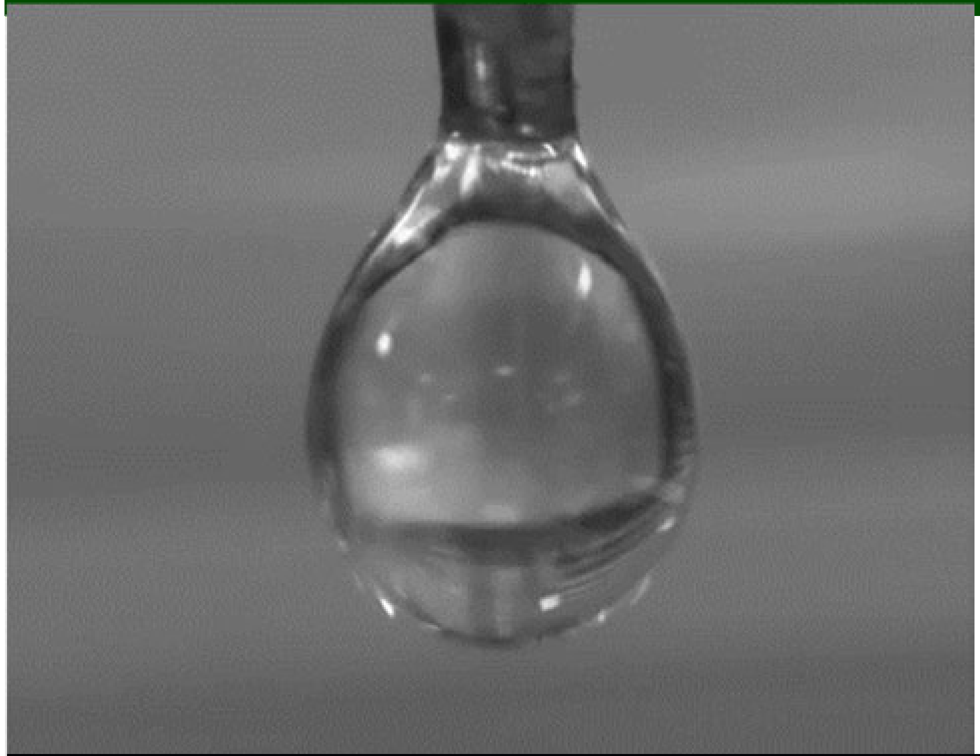

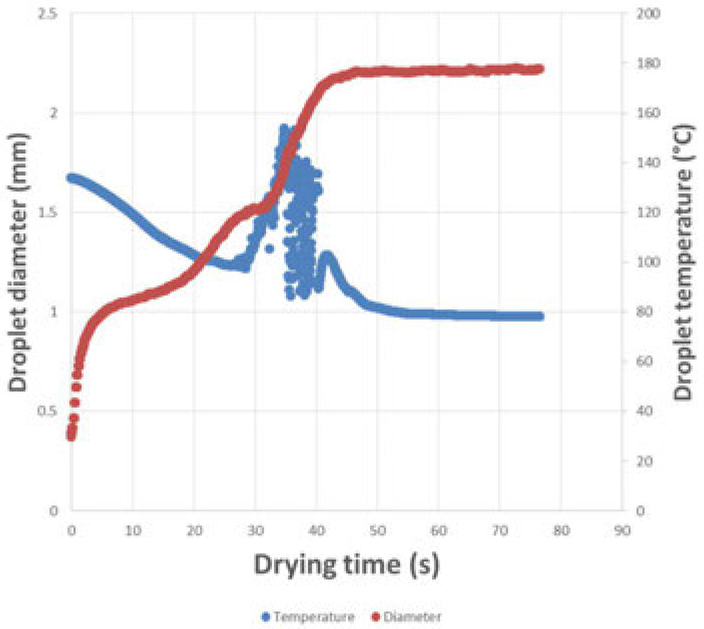

Sucrose - T_{air} = 190 ° C , 45 %, d_{init} = 1.5 mm

inflation/defalation cycles

Silicate Solutions
– particle size larger than drop size

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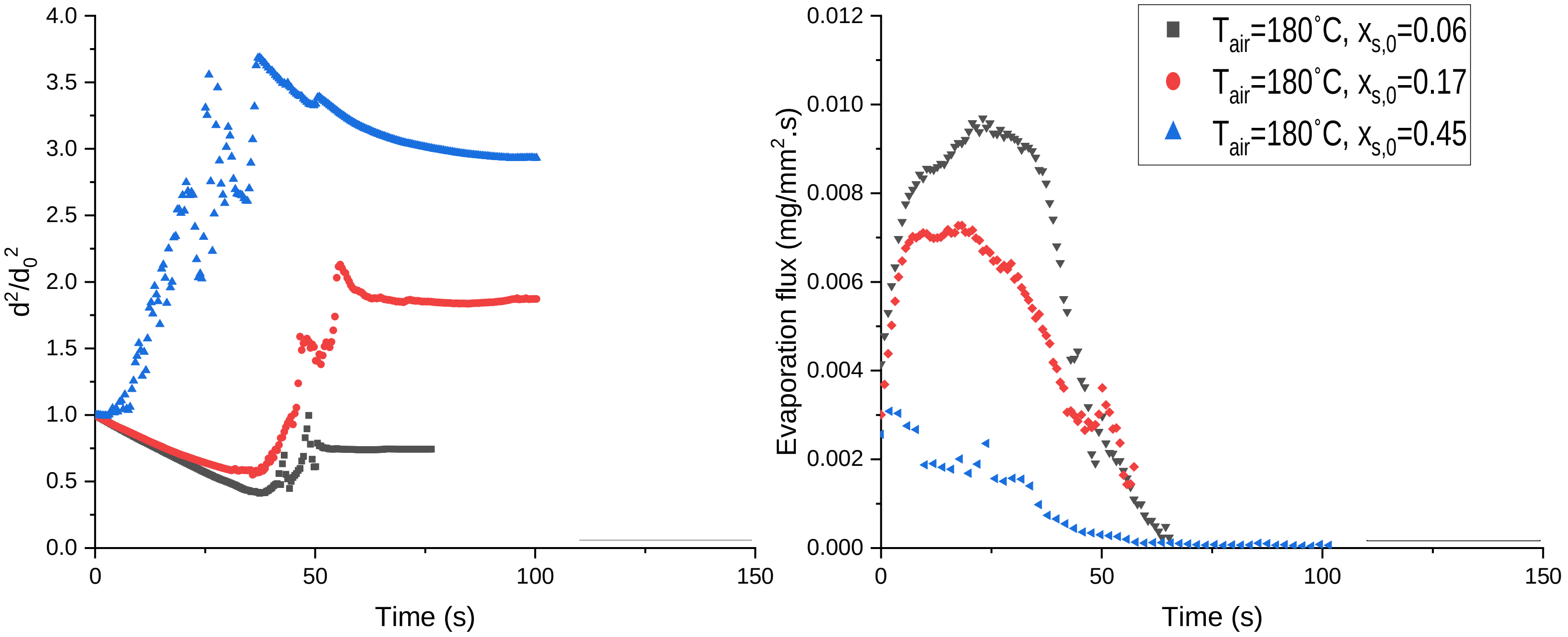

SILICATE SOLUTION at 180˚C, 6%, 17% and 45 % initial concentration

Material Dependence of Morphology Evolutions

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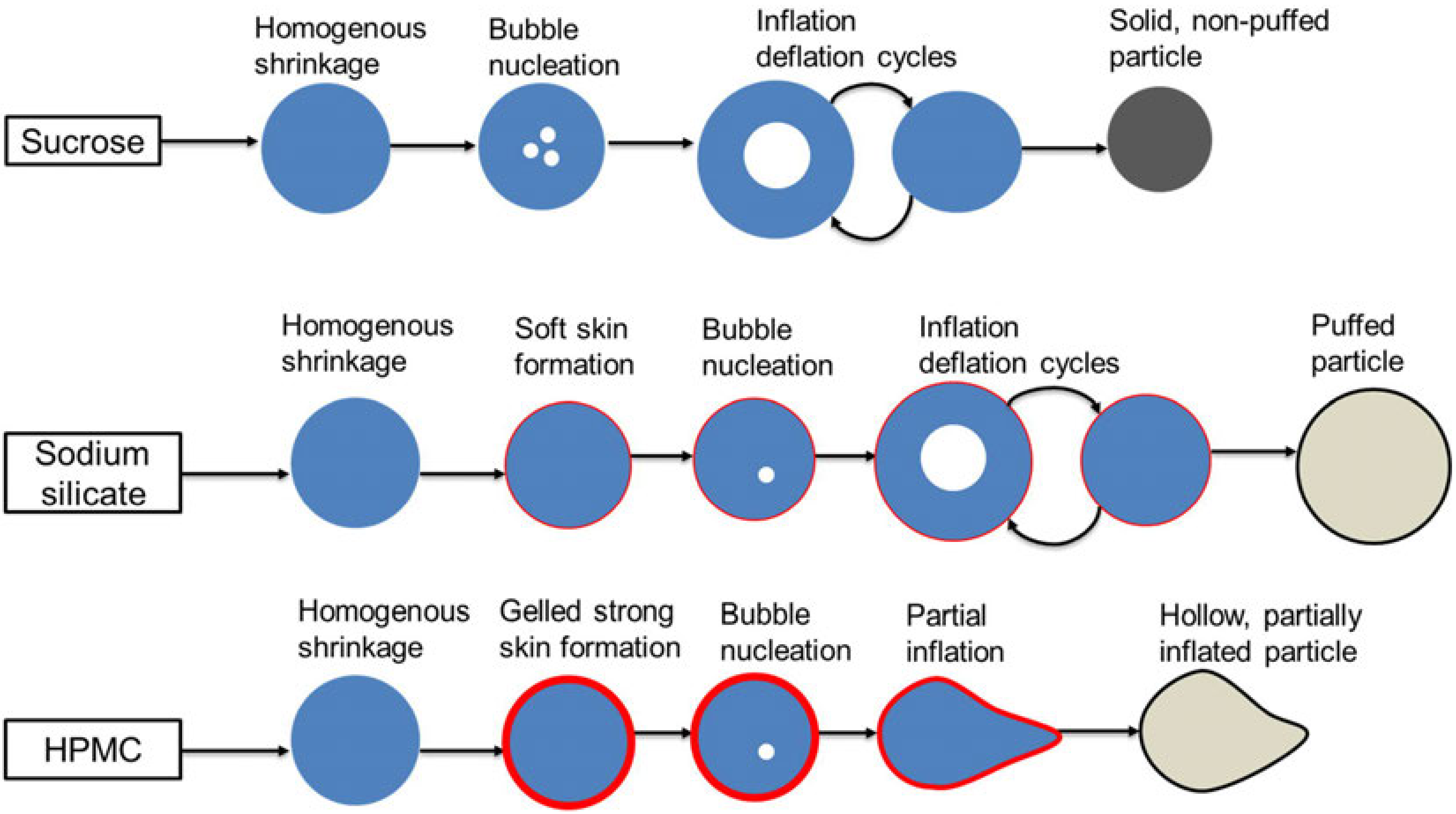

Rupture mechanisms

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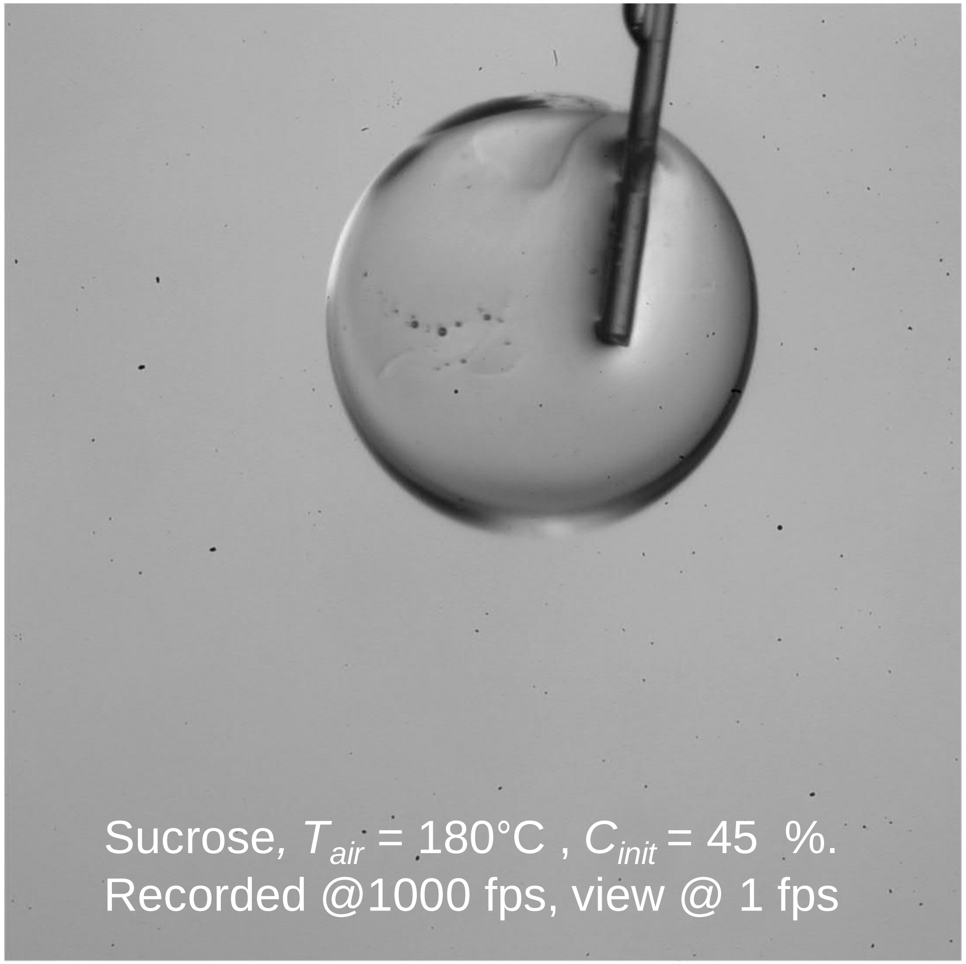
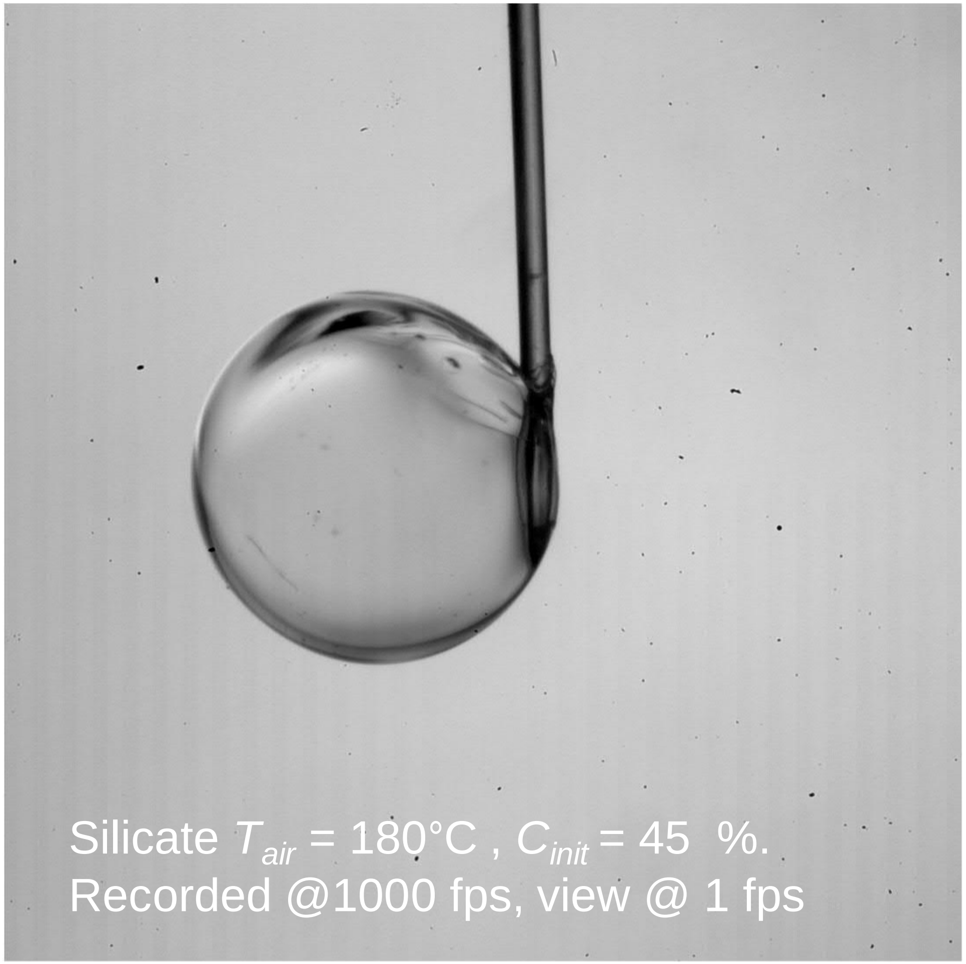
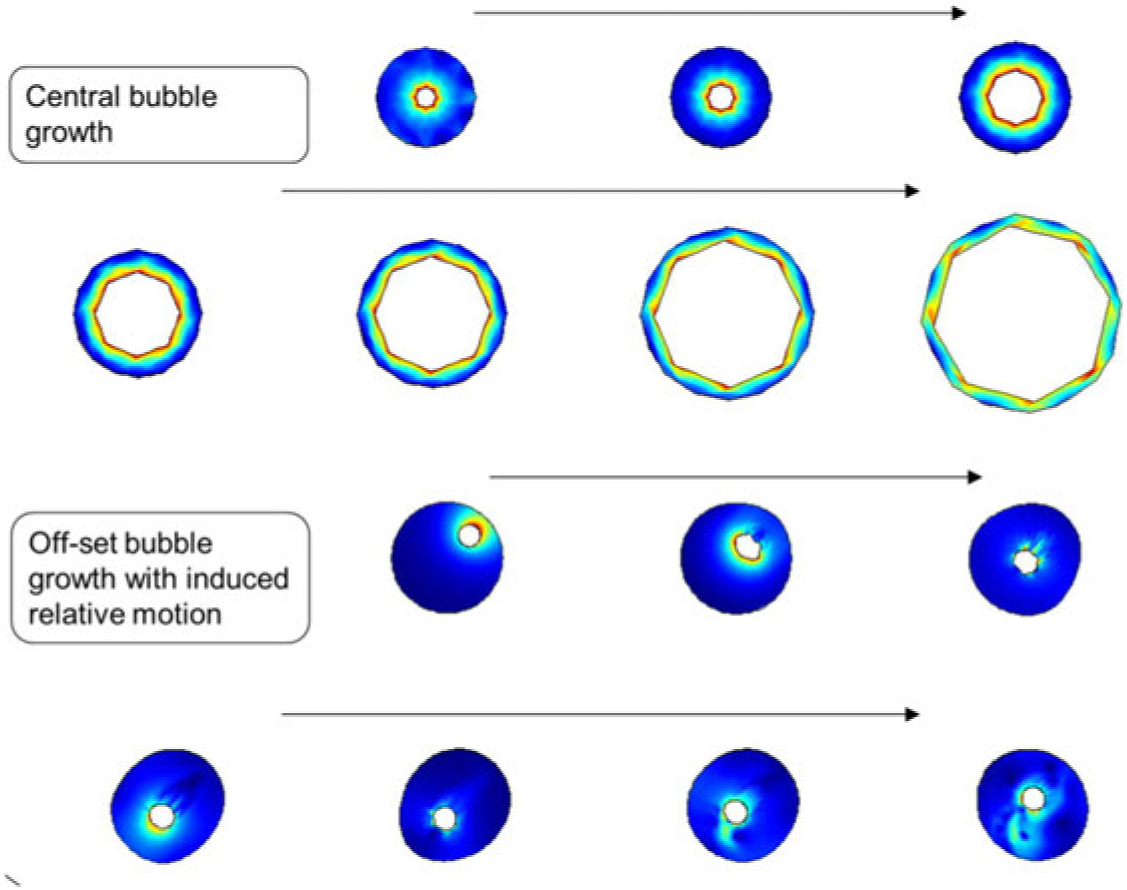


Sucrose, T_{air} = 180°C , C_{init} = 45 %.
Recorded @1000 fps, view @ 1 fps

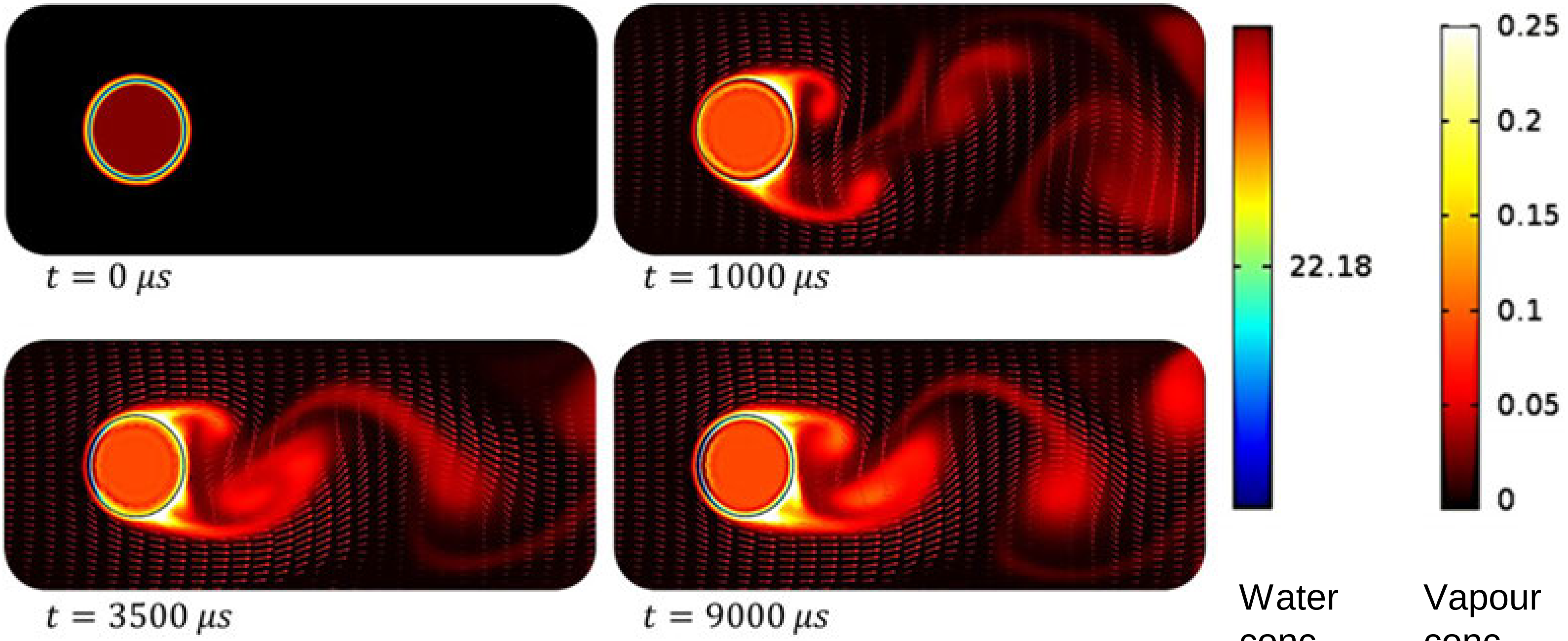


Silicate T_{air} = 180°C , C_{init} = 45 %.
Recorded @1000 fps, view @ 1 fps

2/3-D models of bubble growth in a droplet



Coupling with droplet motion with drying



Water conc (M)

Vapour conc (M)

Colloidal systems
- Ti02 morphology

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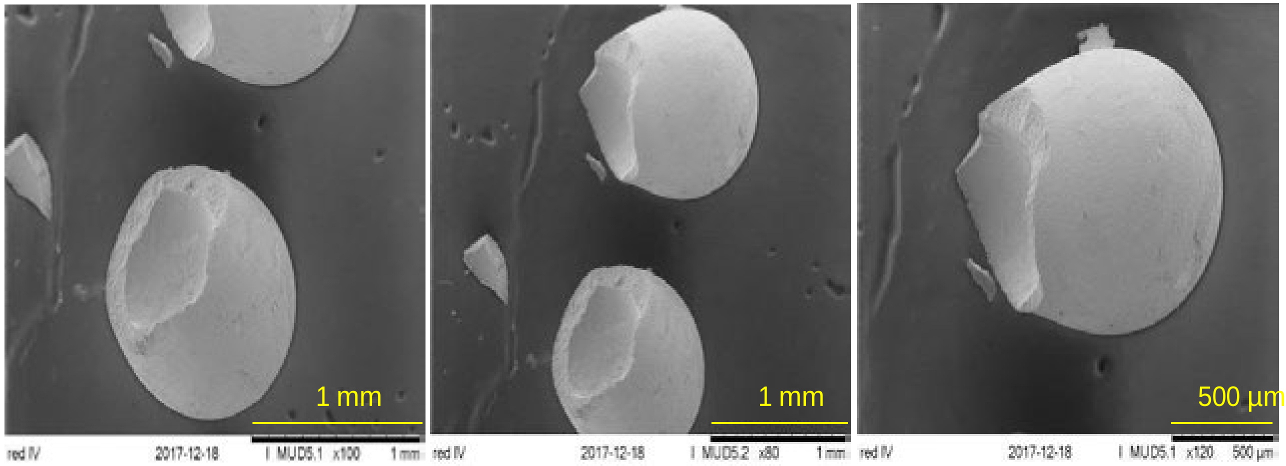
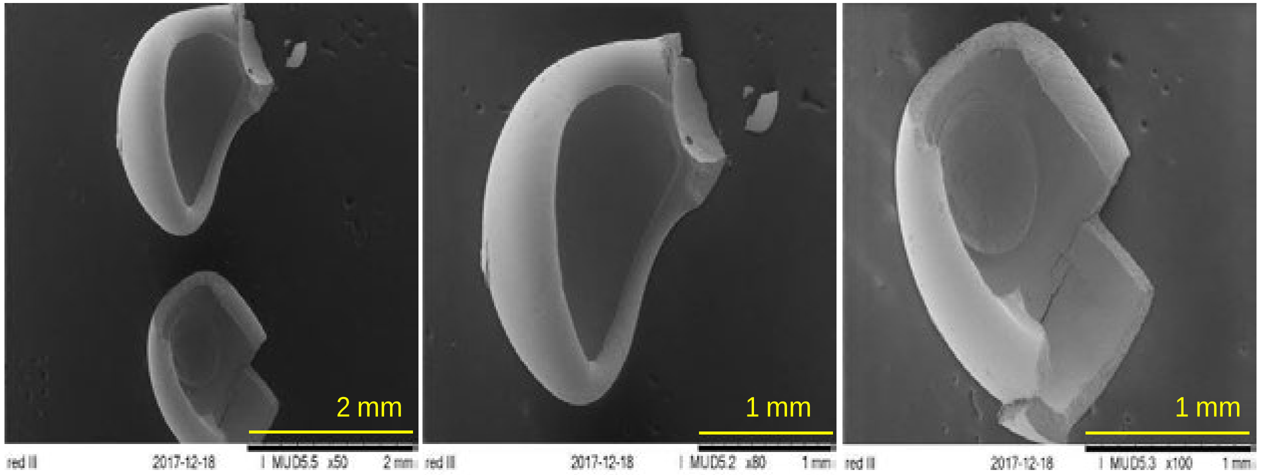
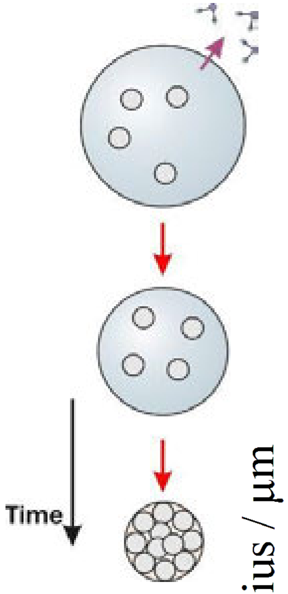
alumina-coated TiO_2 slurry
20%wt
pH=8.4 (IEP)



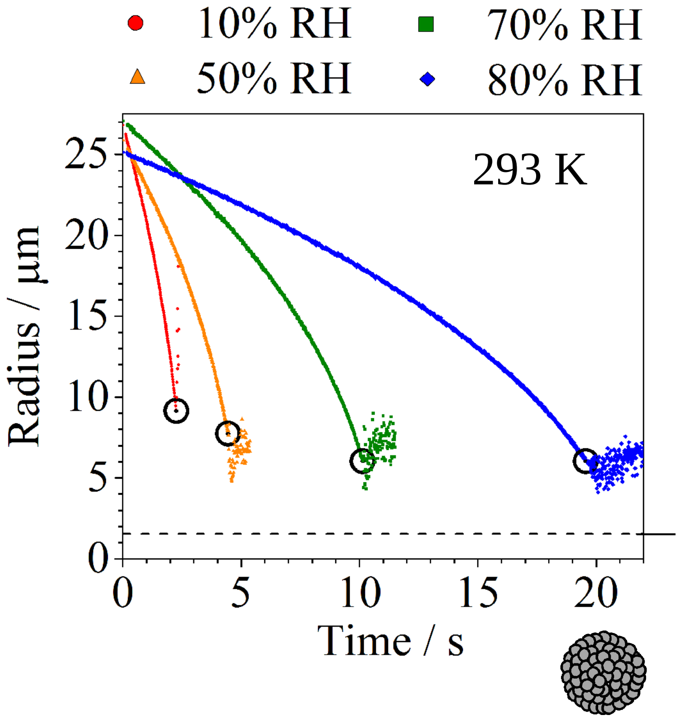
alumina-coated TiO_2
slurry
20%wt
pH=4.5 (non-IEP)



Dependence of Final Size on Drying Rate

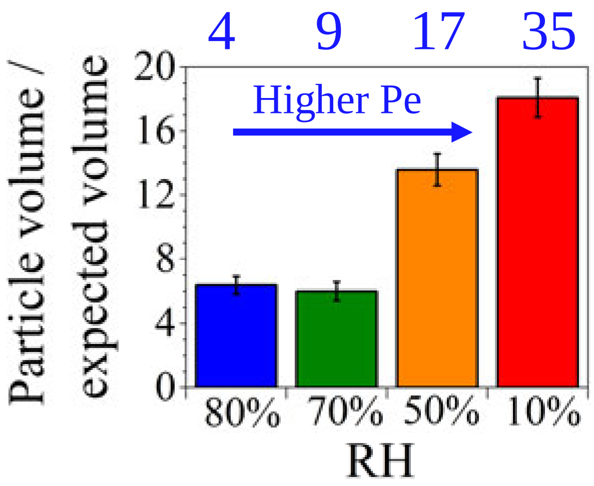


Droplets containing 0.1 % volume of silica hydrophilic nanoparticles.



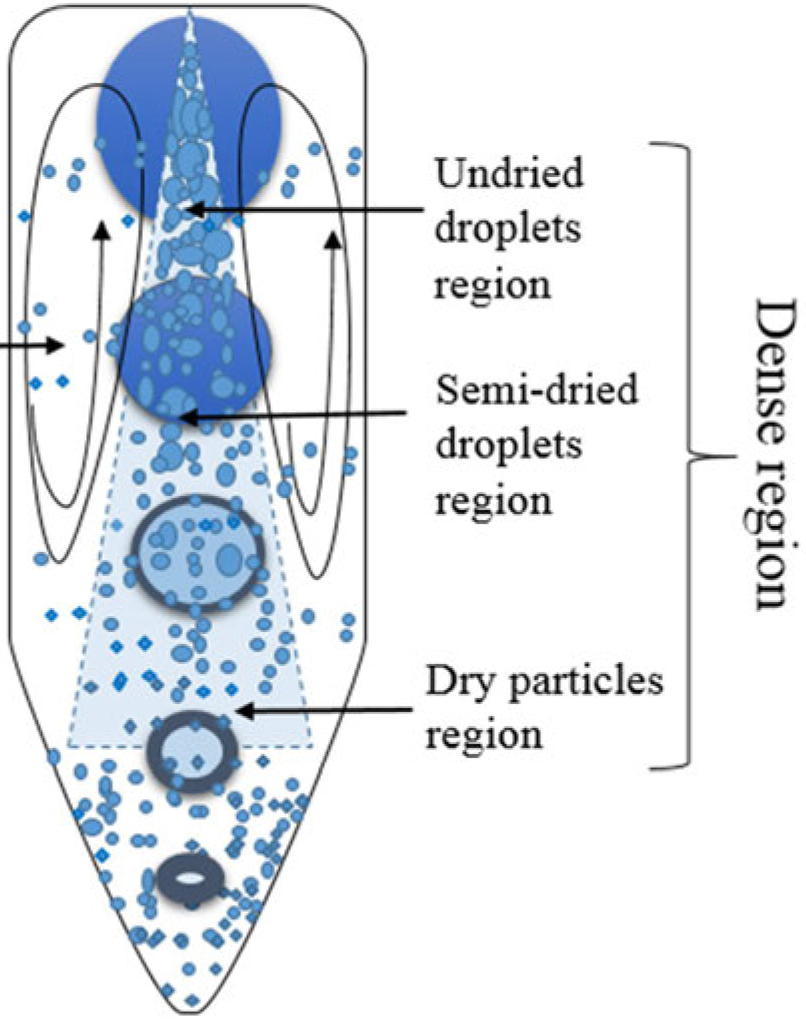
Expected final solid-particle radius (including exclude volume)

$$Pe = \frac{\text{Evaporation rate}}{\text{Diffusional mixing rate}}$$



Final particle volumes suggest the particles are less dense at higher drying rate

Spray Drying



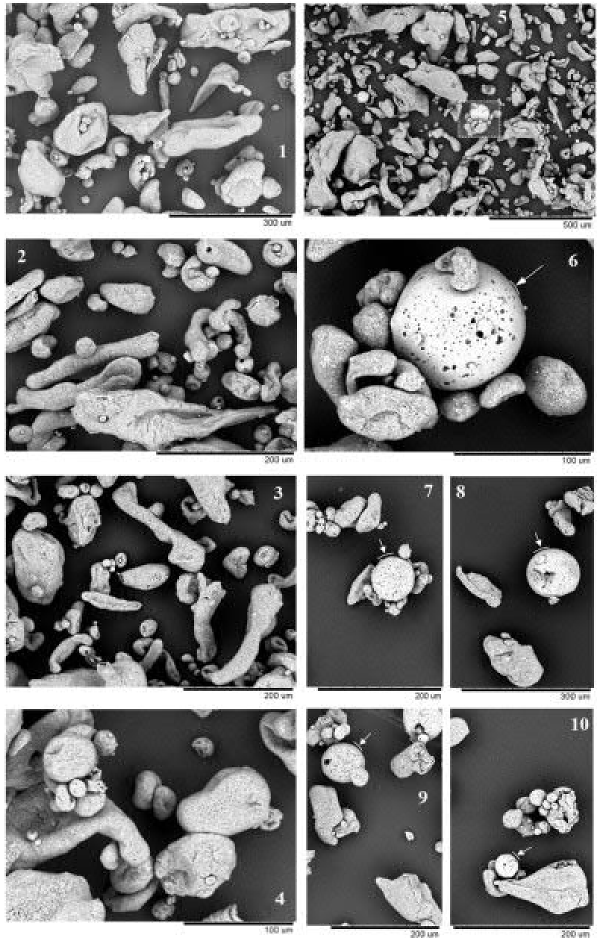
Recalculations

Undried droplets region

Semi-dried droplets region

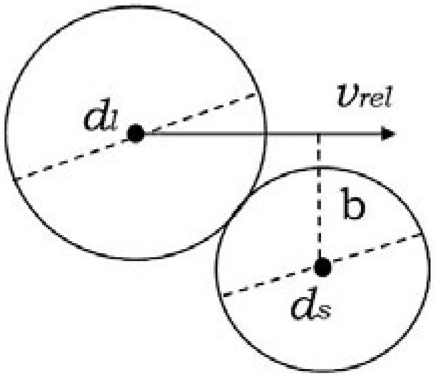
Dry particles region

Dense region



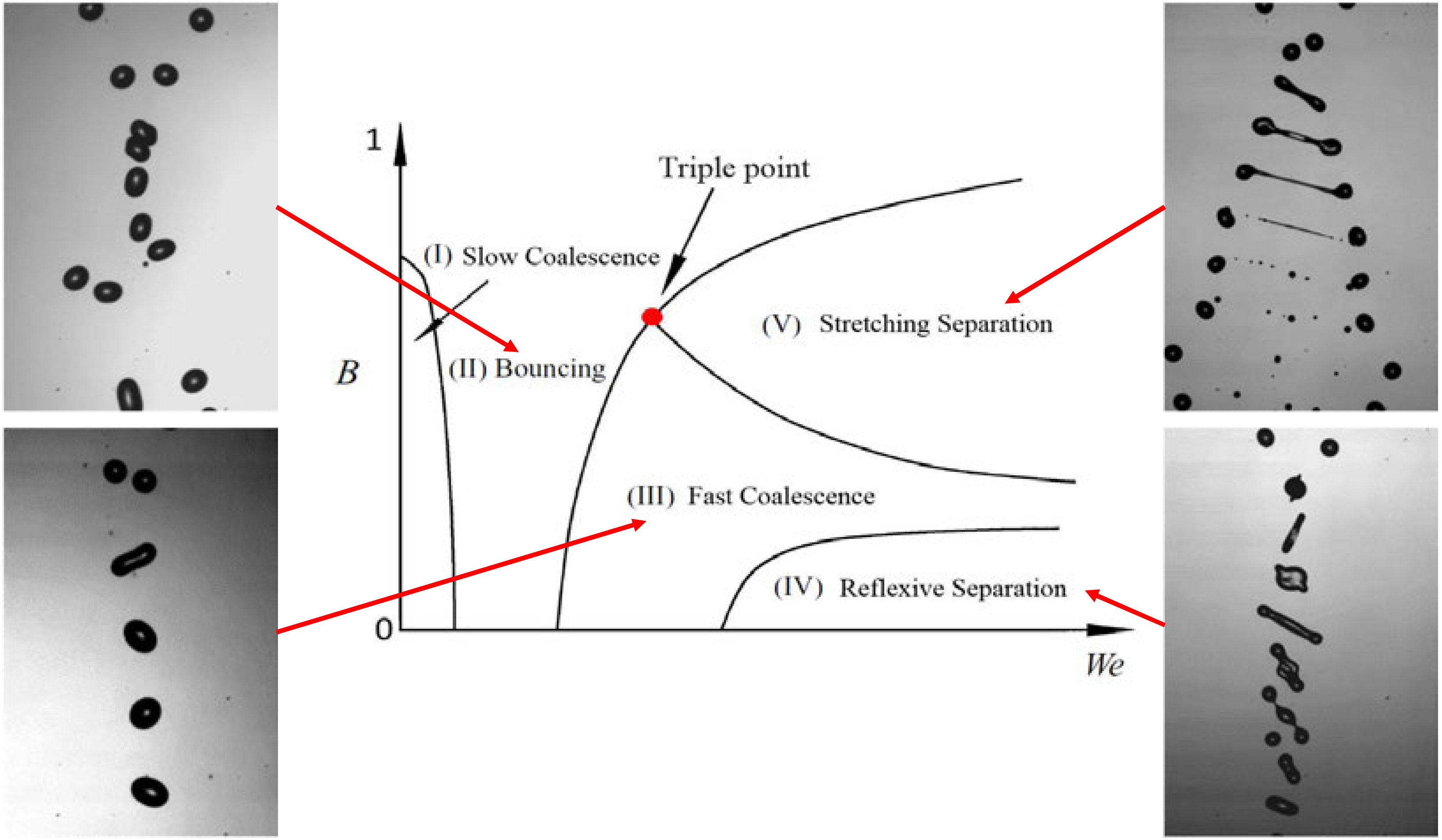
Francia et al. (2016)

Collisions Outcomes and Regime Maps

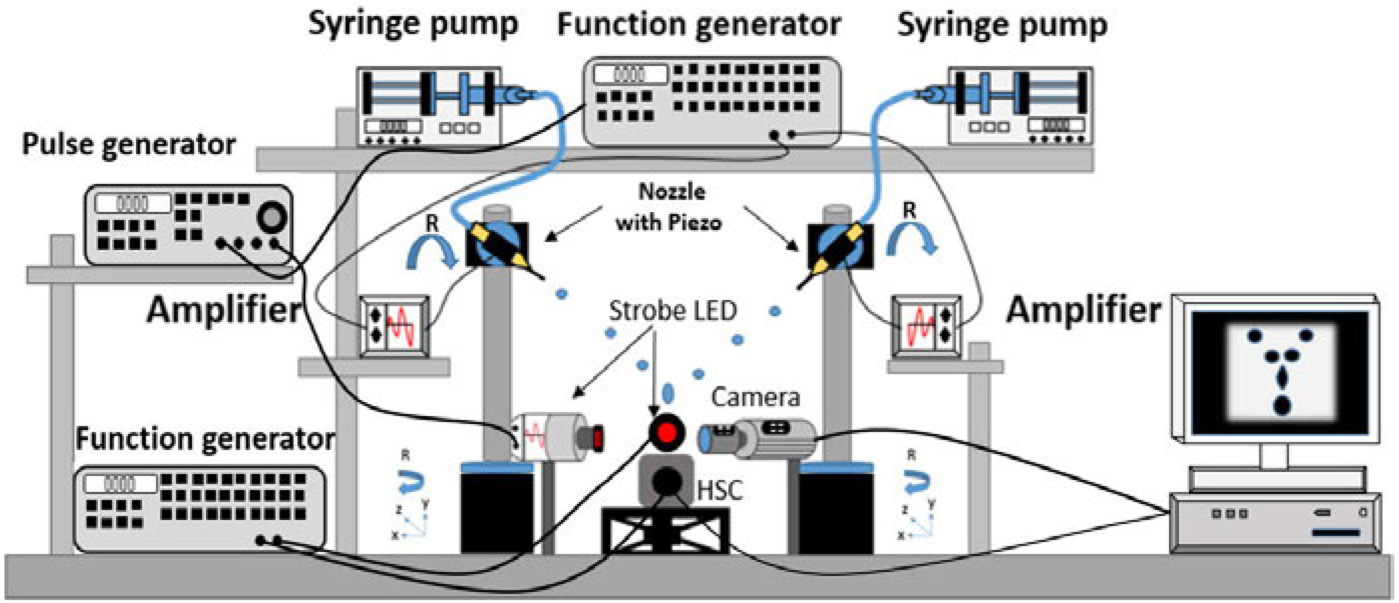


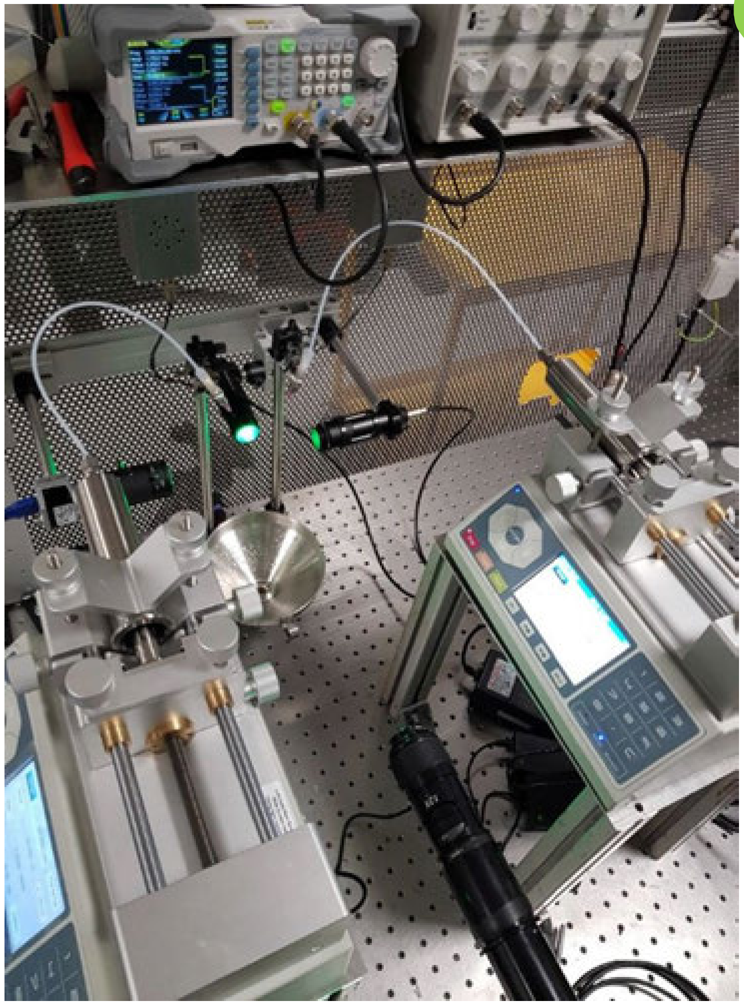
$$B = \frac{2b}{d_s + d_l}$$

$$We = \frac{E_k}{E_s} = \frac{\rho d_s v_{rel}^2}{\sigma}$$



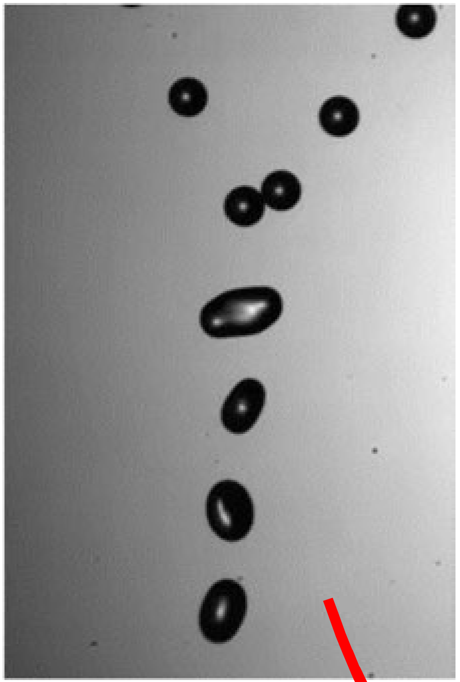
The Rig

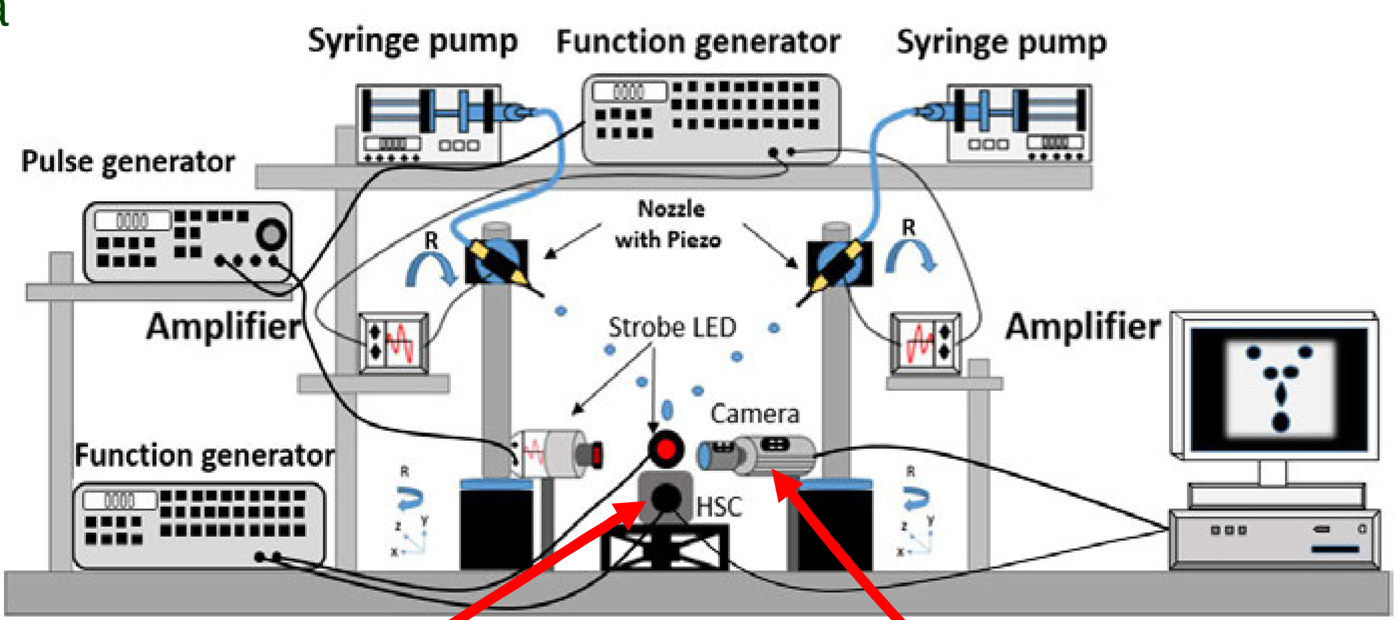

Syringe pump
Function generator
Syringe pump
Pulse generator
Nozzle with Piezo
R
R
Amplifier
Strobe LED
Amplifier
Camera
Function generator
HSC
R
z
y
x
R
z
y
x



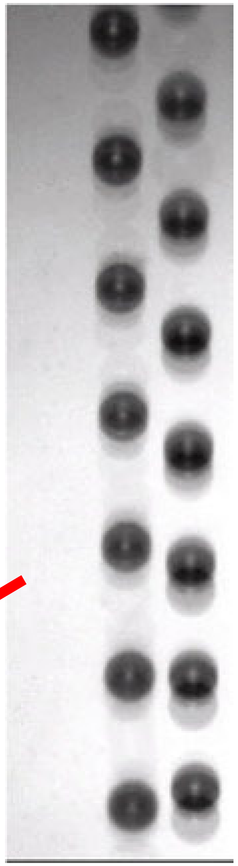
The Rig

High-speed Camera





Strobe imaging



HPMC Regime Maps

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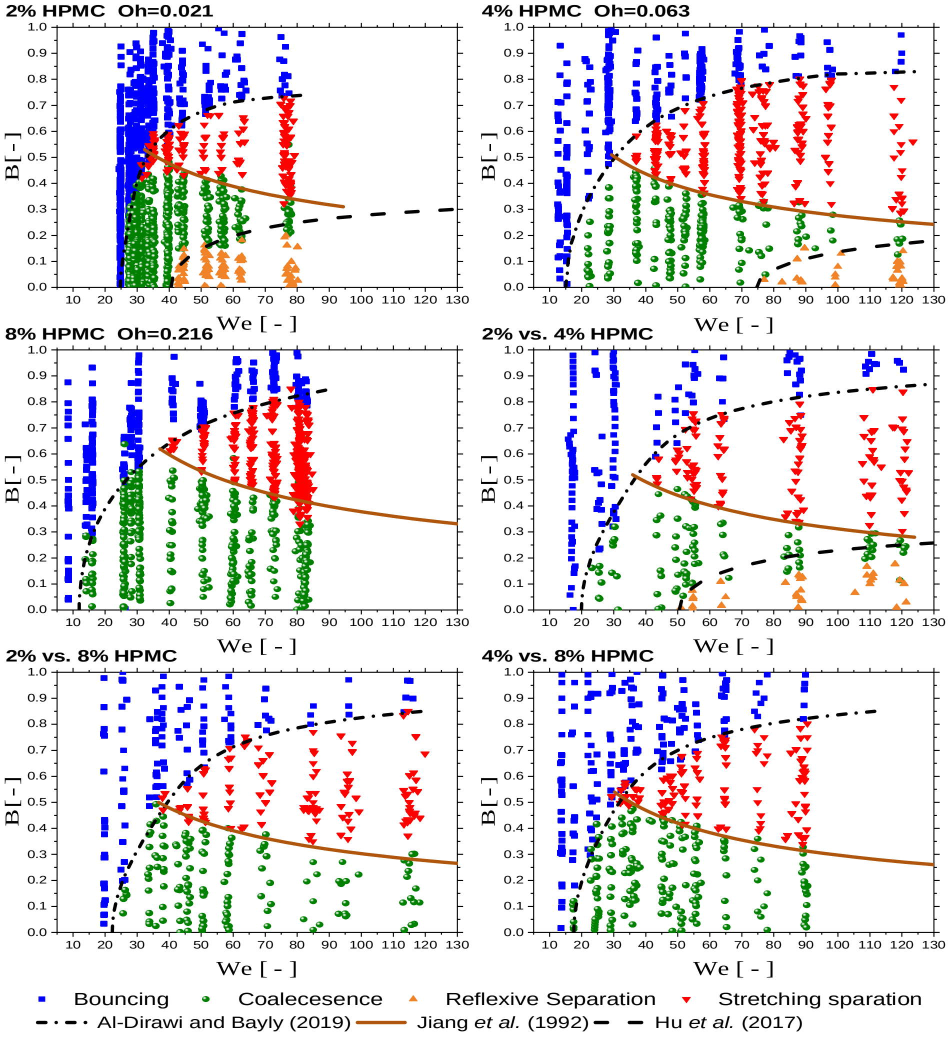


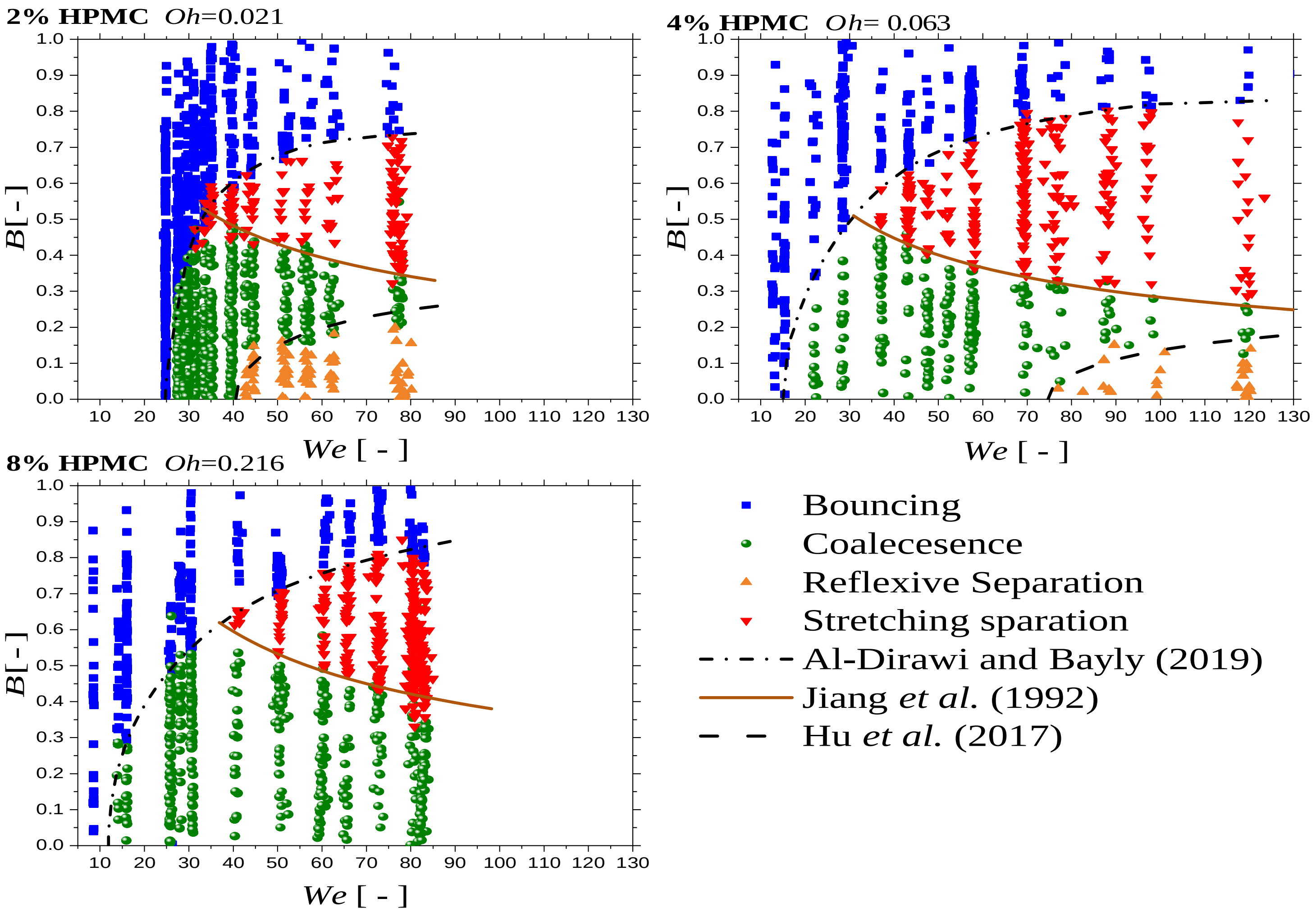
Type of liquid	**ρ** (kg m^{-3})	***σ*** (mN m^{-1})	**μ** (mPa s)
2% HPMC	998	46	2.8
4% HPMC	998	45.8	8.2
8% HPMC	997	45.72	28.4

$$d = 360 \pm 10 \mu m$$

HPMC: hydroxypropyl methylcellulose (polymer)

Al-Dirawi, K.H. and Bayly, A.E., 2019. **A new model for the bouncing regime boundary in binary droplet collisions**. *Physics of Fluids*, *31*(2), p.027105.

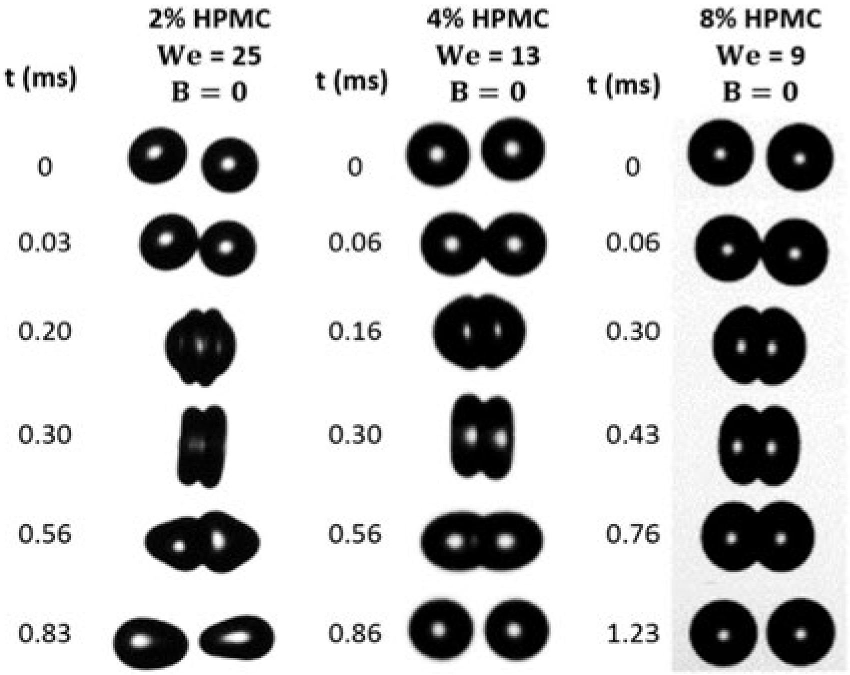
HPMC Regime Maps – equal size and viscosity



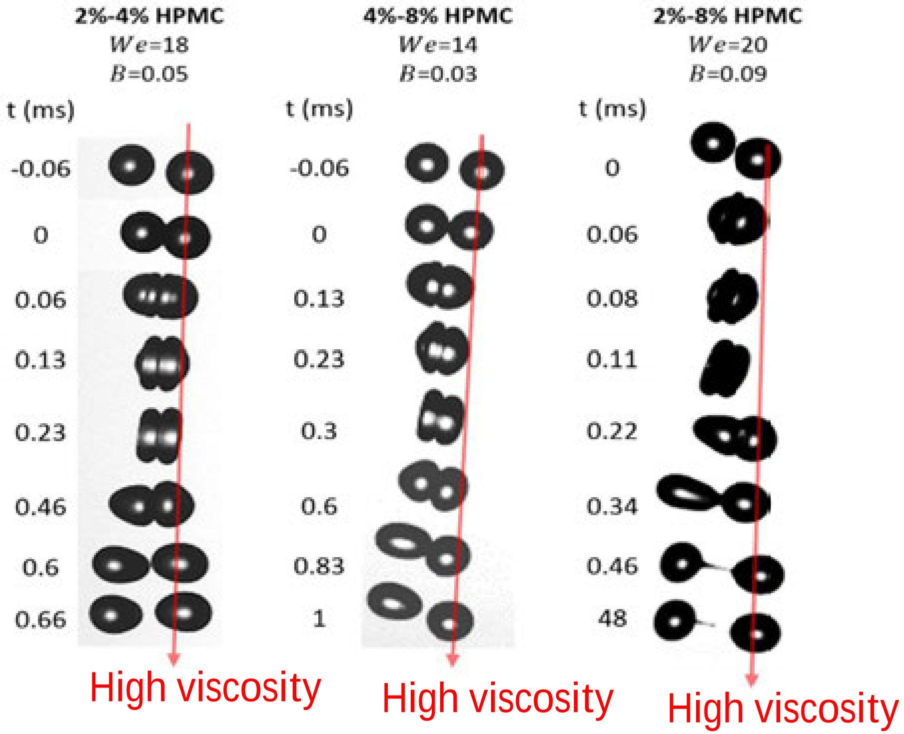
- Typical regime maps seen for all viscosities
- Viscosity moves the boundaries, most noticeably - loss of reflexive separation in high viscosity case
- Literature models capture the boundaries

Bouncing

Identical viscosity



Non-identical viscosity

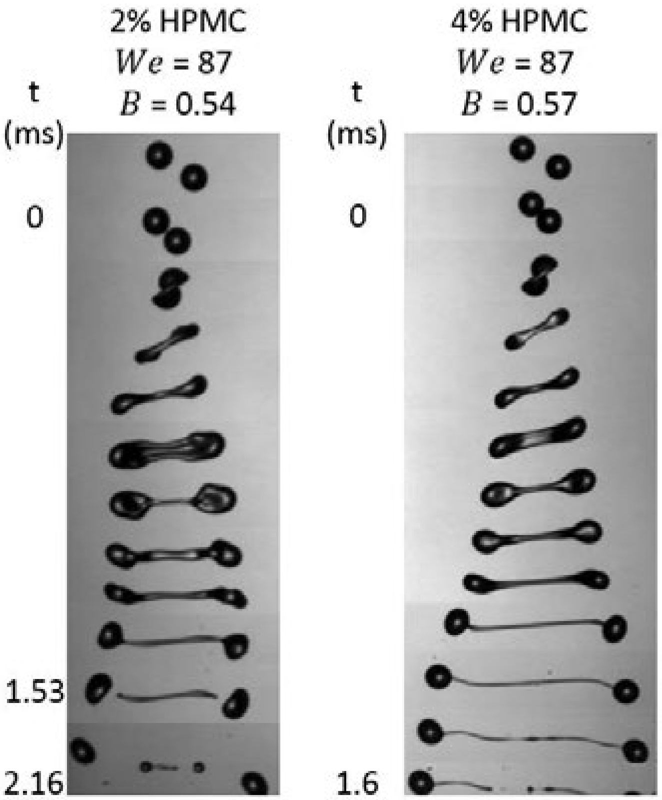


- Increasing the viscosity decreases the deformation and hence promotes coalescence.

- The viscosity difference between the colliding droplet causes deformation difference which in turns leads to an intermediate critical We compared to the identical cases.

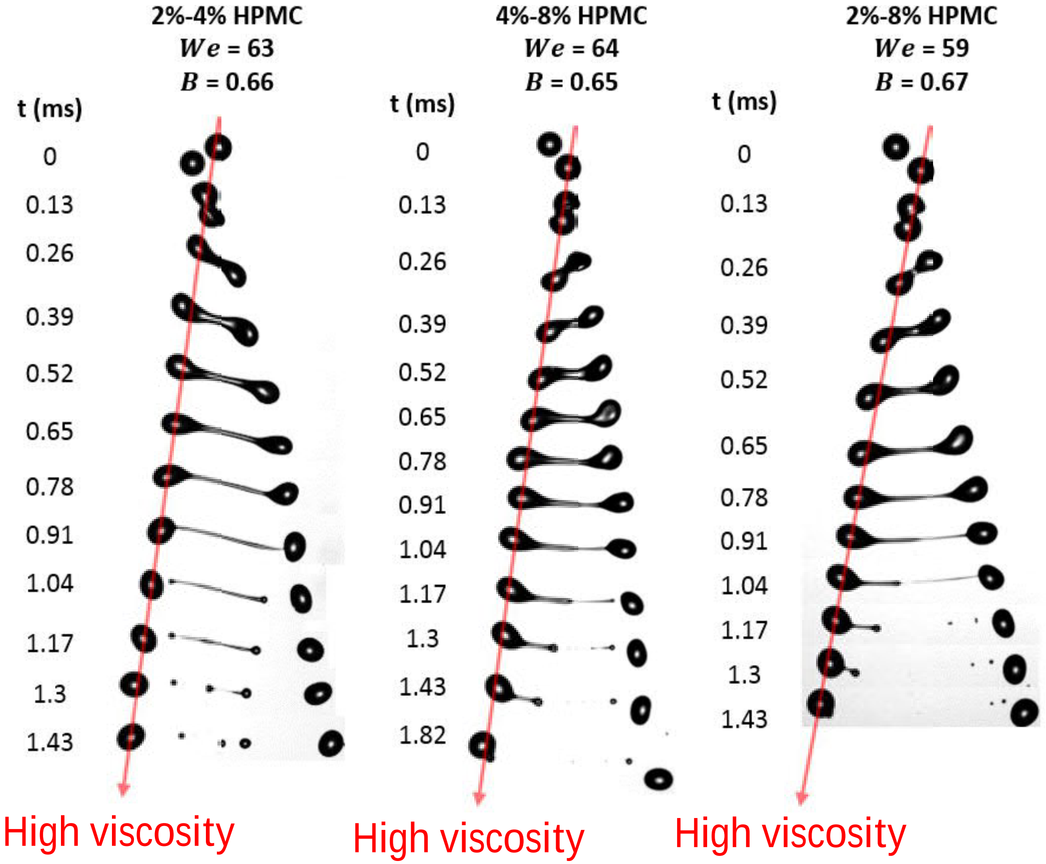
Stretching separation

Identical viscosity



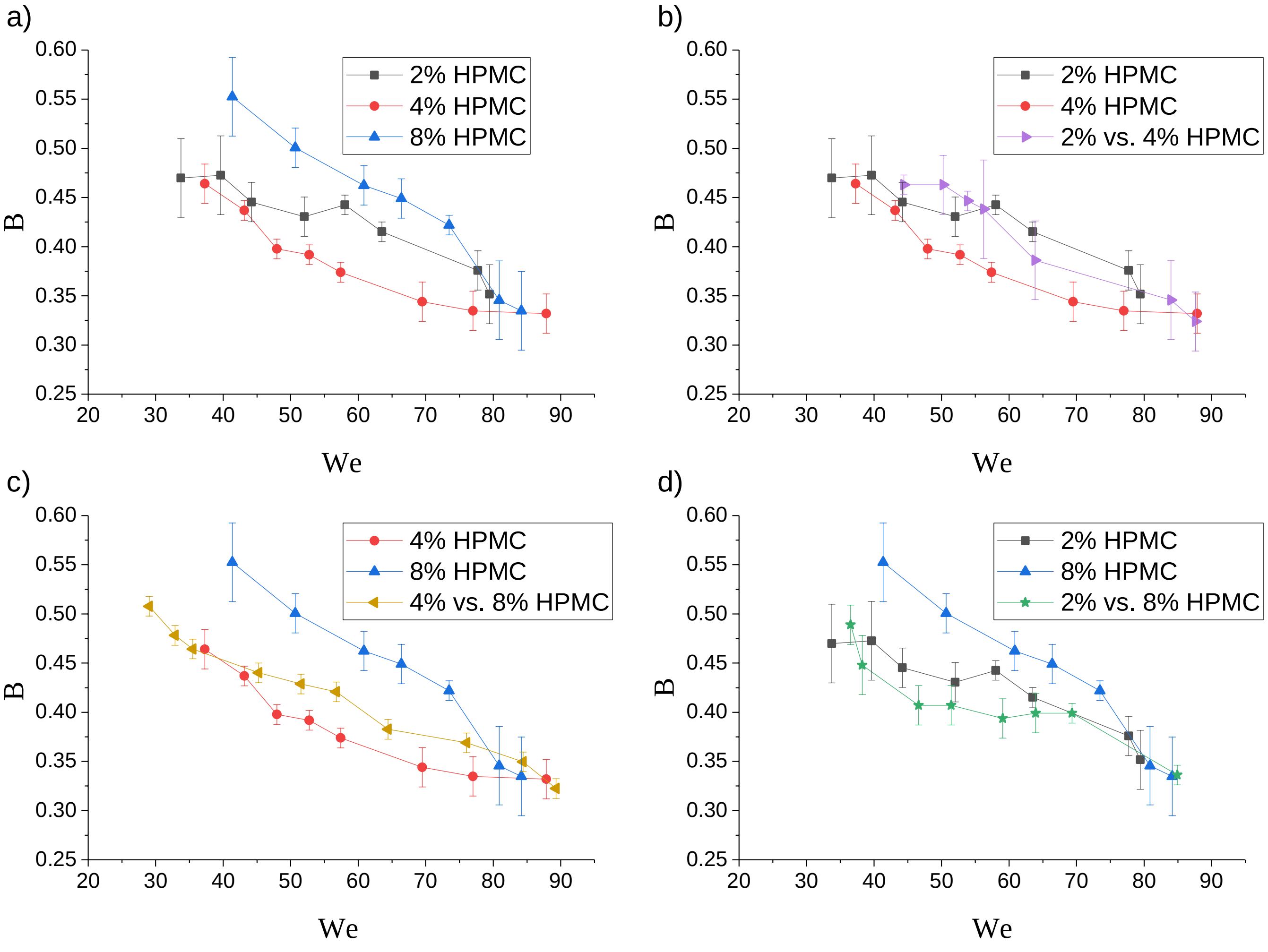
- ❖Uniform ligament

Non-identical viscosity



- ❖Non uniform ligament

Stretching separation

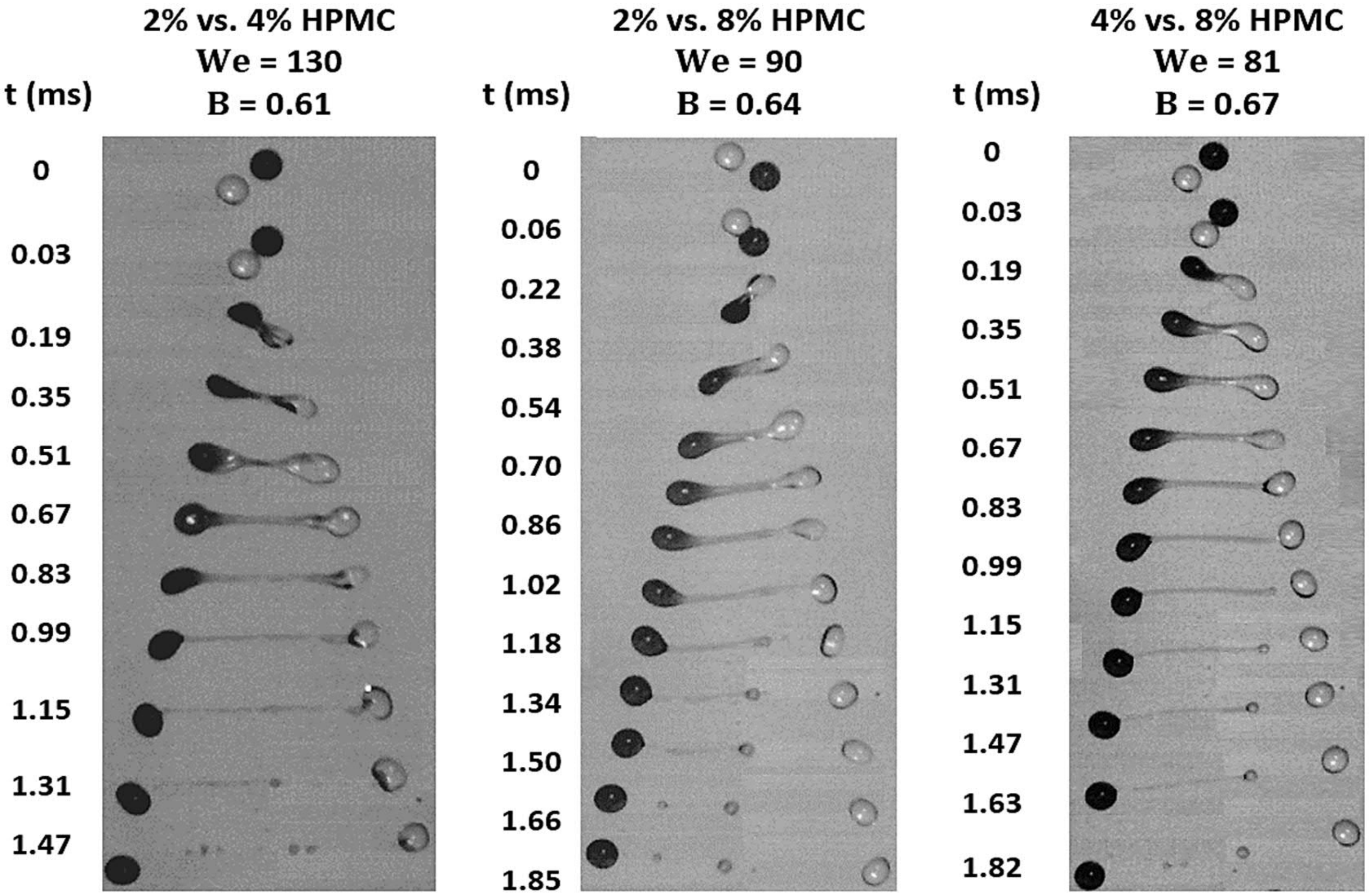


- ❖In identical collisions, increasing the viscosity shifts the boundary upwards.

- ❖In non-identical collisions, the boundary is superimposed on the identical case of the low viscosity droplet.

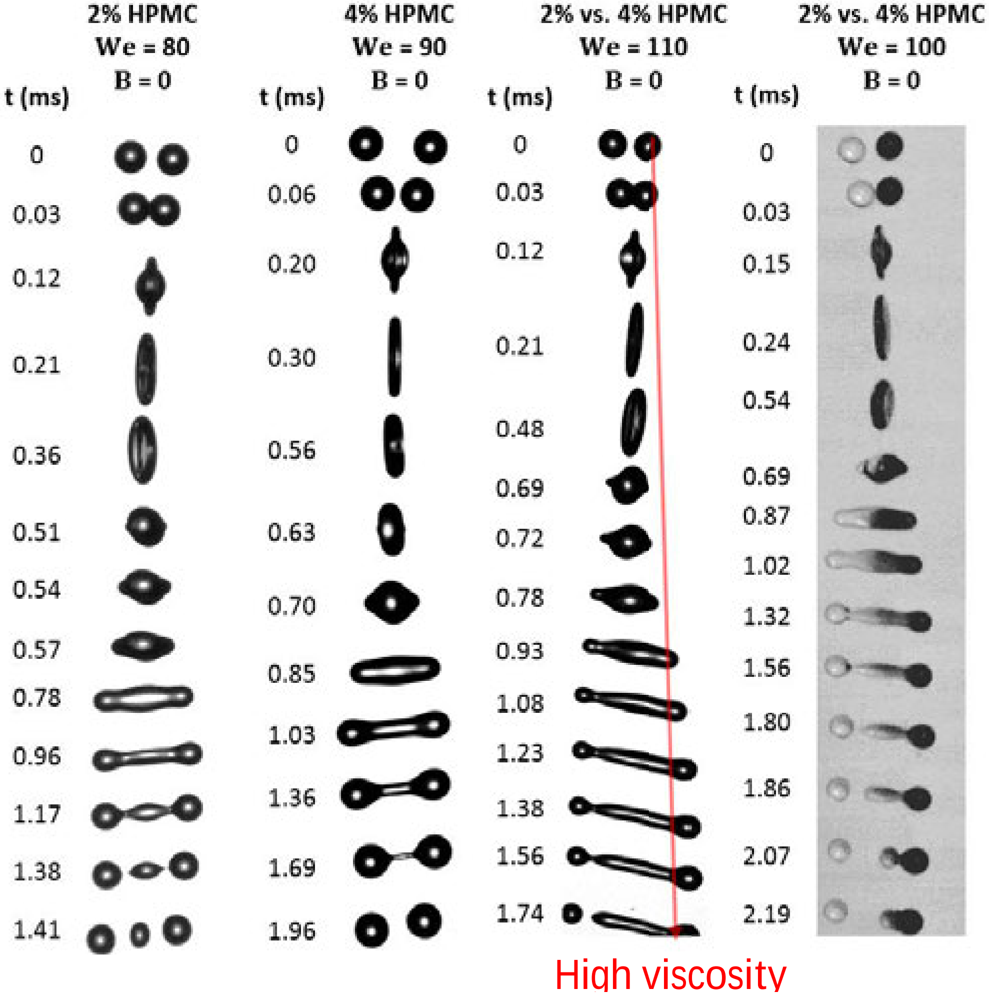
Why?

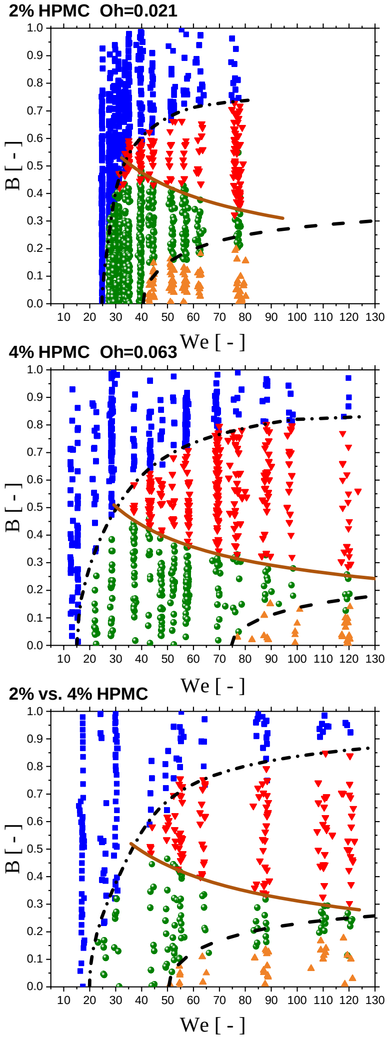
Stretching separation (coloured images)



- ❖ The ligaments are mainly from the lower viscosity droplet.
- ❖ There is no significant mixing between the colliding droplets

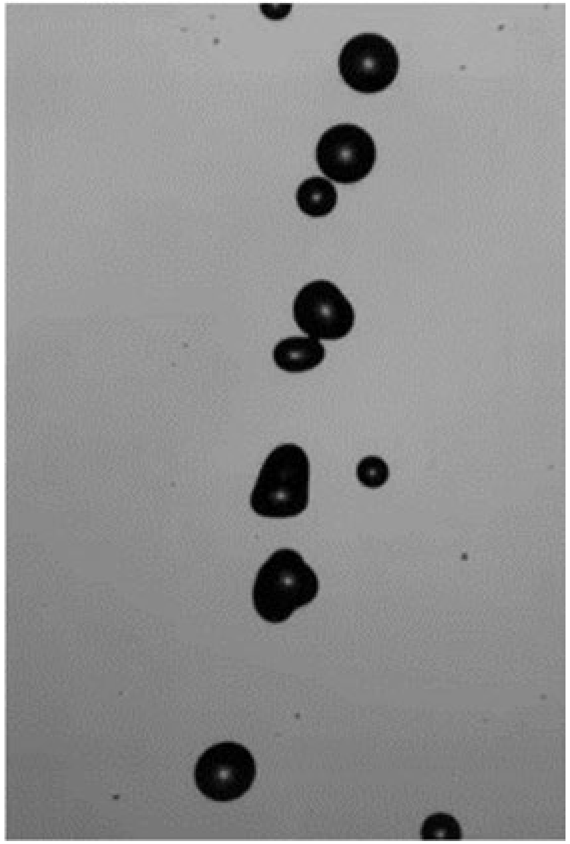
Reflexive separation (different viscosities)

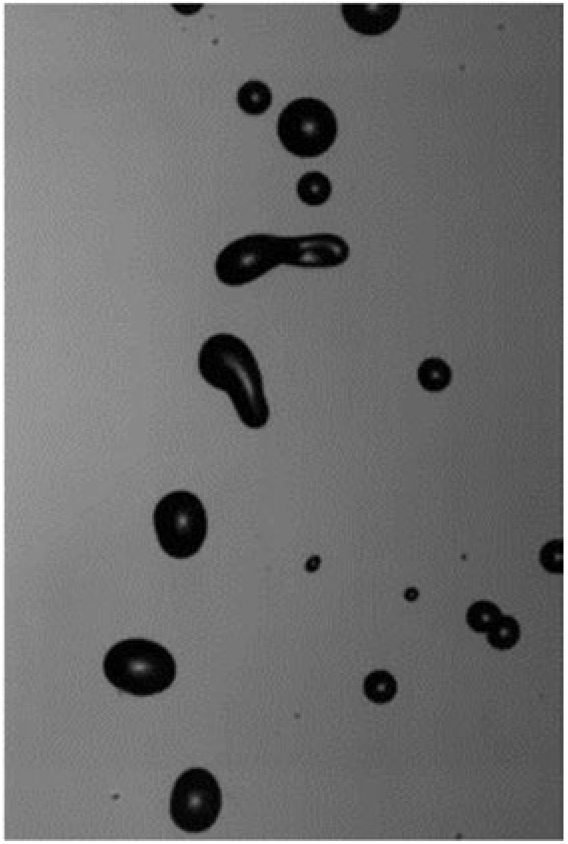


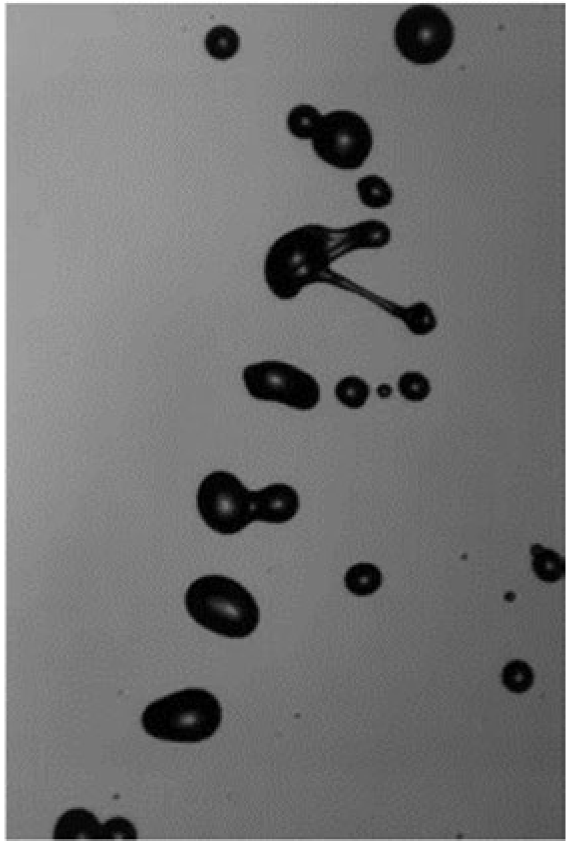


- ❖ The reflexive separation has an intermediate We compared to the identical cases.
- ❖ There is a mixing in the ligaments but the reflexed droplets have no mixing.
- ❖ After separation:
  - small droplet with low viscosity;
  - large droplet with mixed droplet;

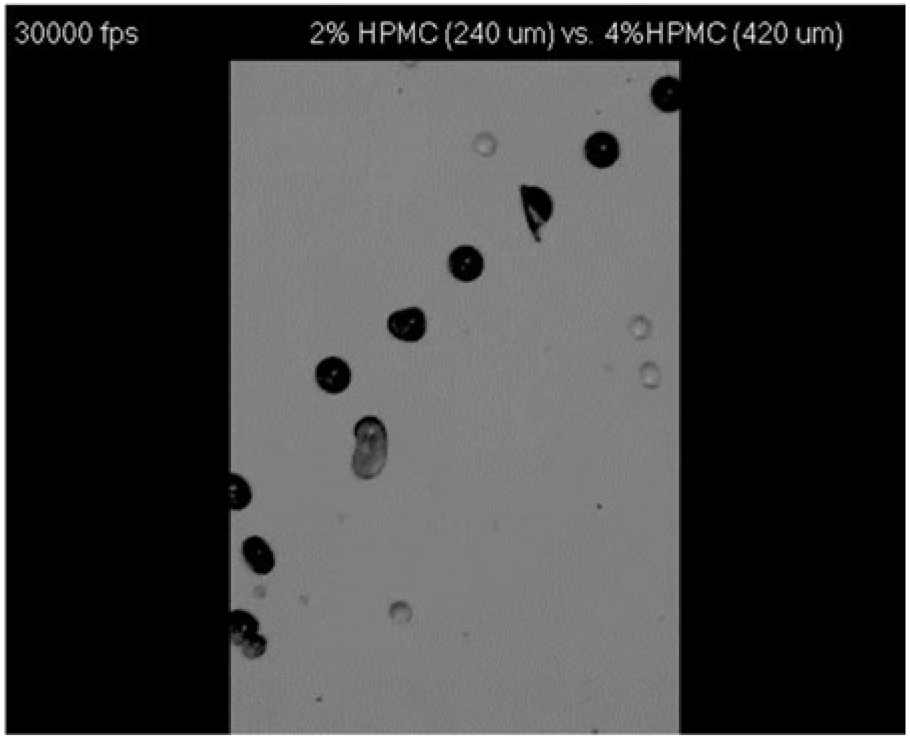
Different size collisions of 2%HPMC

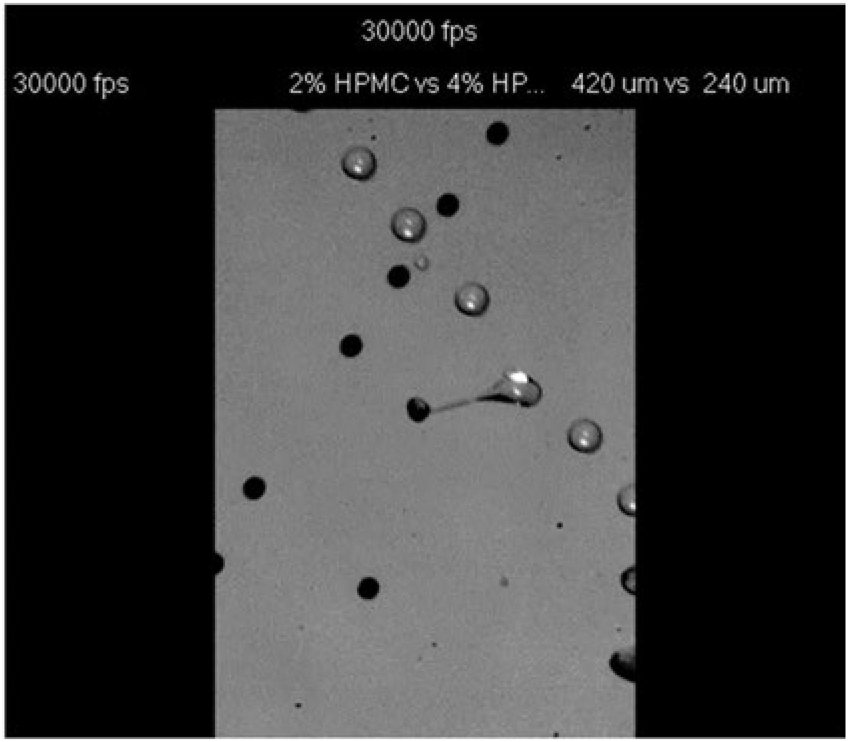

Bouncing


Coalescence and Stretching Separation


Reflexive separation

Different size, different viscosity





Conclusions

Collisions of droplets with Identical and non-identical viscosity have been conducted experimentally.

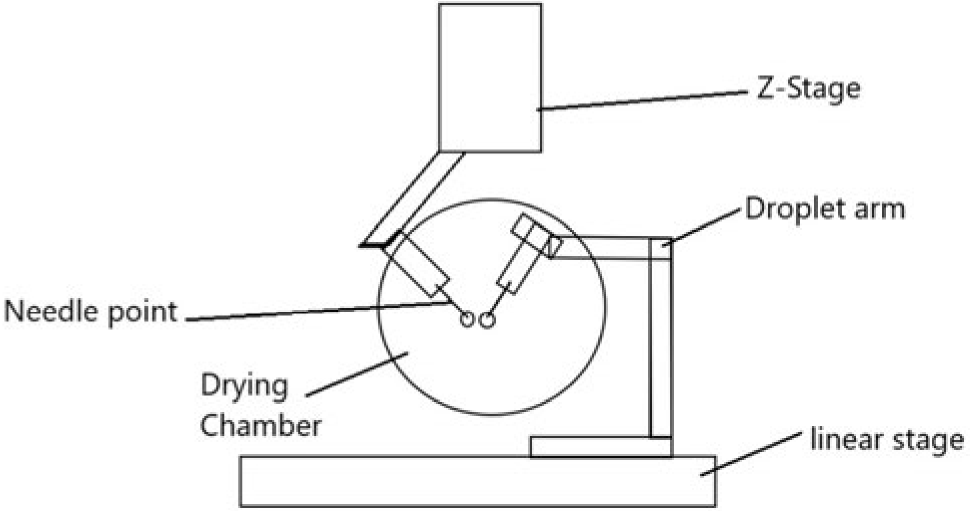
Identical viscosity:

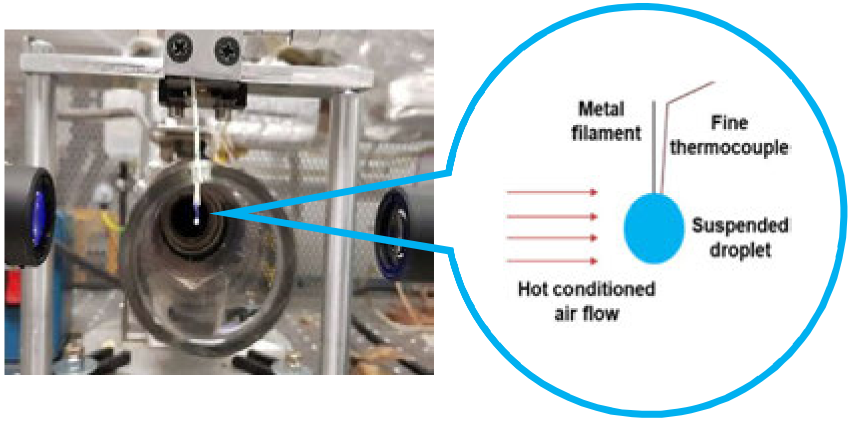
- Increasing the viscosity shifts the bouncing regime towards lower We.
- Increasing the viscosity shifts the stretching separation regime towards higher B.
- Increasing the viscosity shifts the reflexive separation regime towards higher We.

Non-Identical viscosity:

- The boundaries of bouncing and reflexive separation take an intermediate position.
- The boundaries of the stretching separation is comparable to the identical case of the low viscosity droplet.

CONTACT DYNAMICS OF DRYING DROPLETS





Motion controlled via motorized linear stage

Control of
- position,
- ‘collision’ velocity,
- contact time

CONTACT DYNAMICS OF DRYING DROPLETS

SUMMER PROJECT

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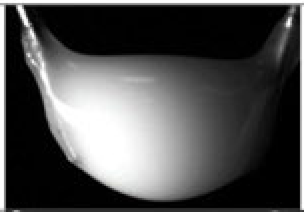
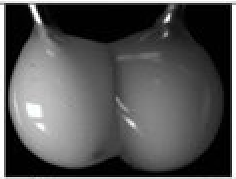
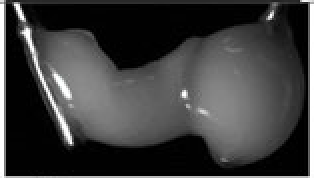
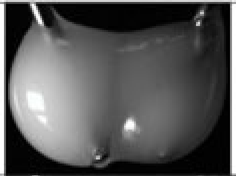
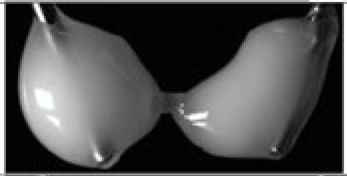
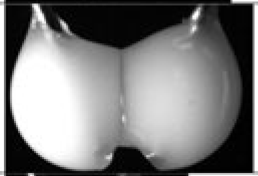
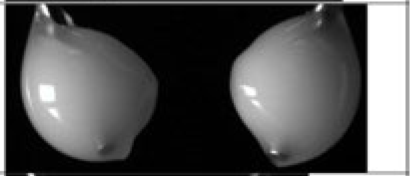
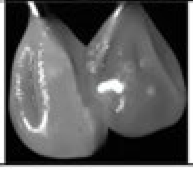
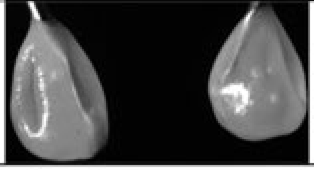
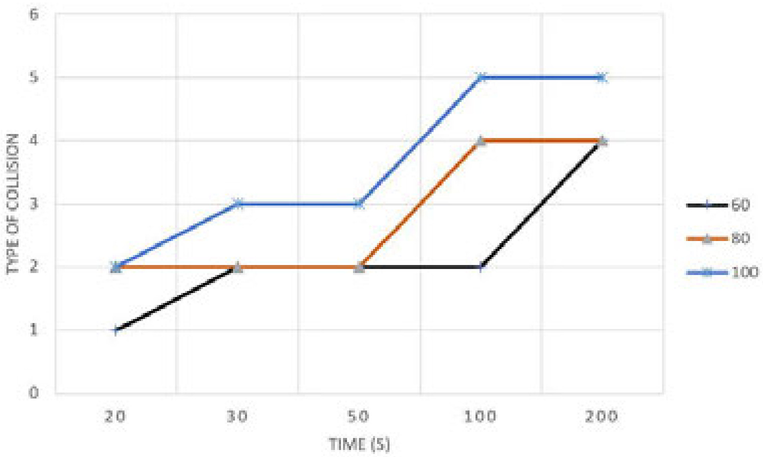
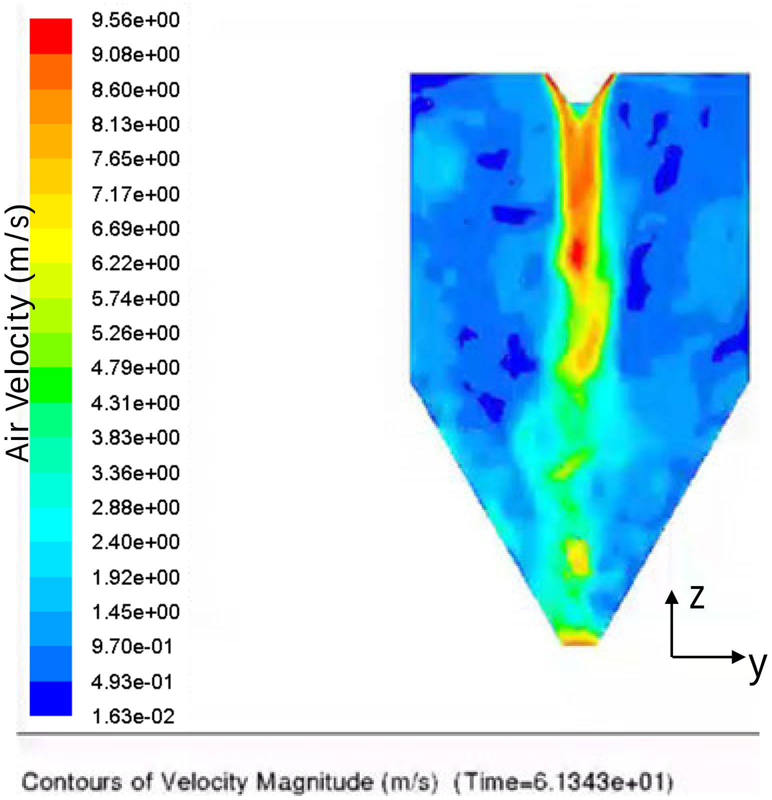
Type of collision	During	After
Coalescence 1		
Adhesive 2		
Equally adhesive and cohesive 3		
Tacky crust and cohesive 4		
Not sticky 5		

- Mechanisms identified and characterized.
- Behaviours mapped

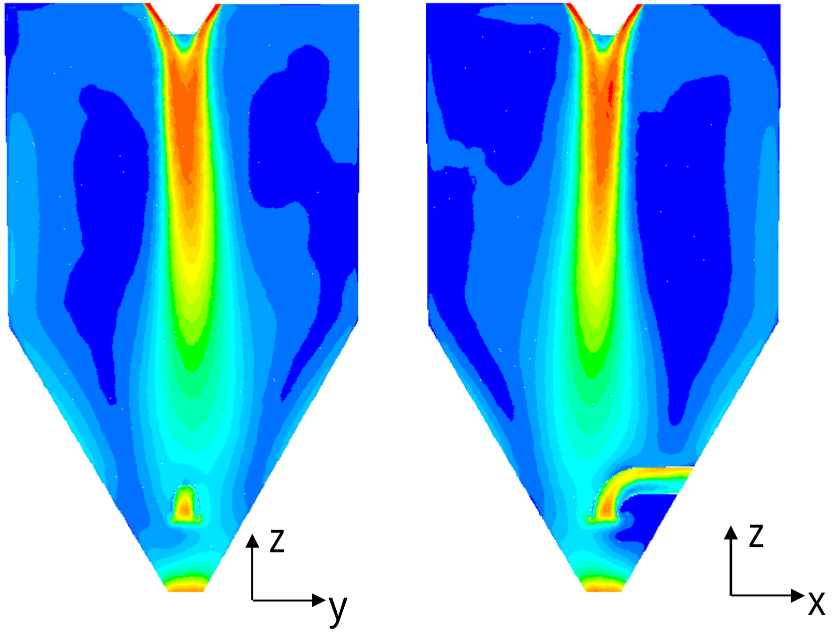


Contours of Air Flow Profile

Animation of Air Flow



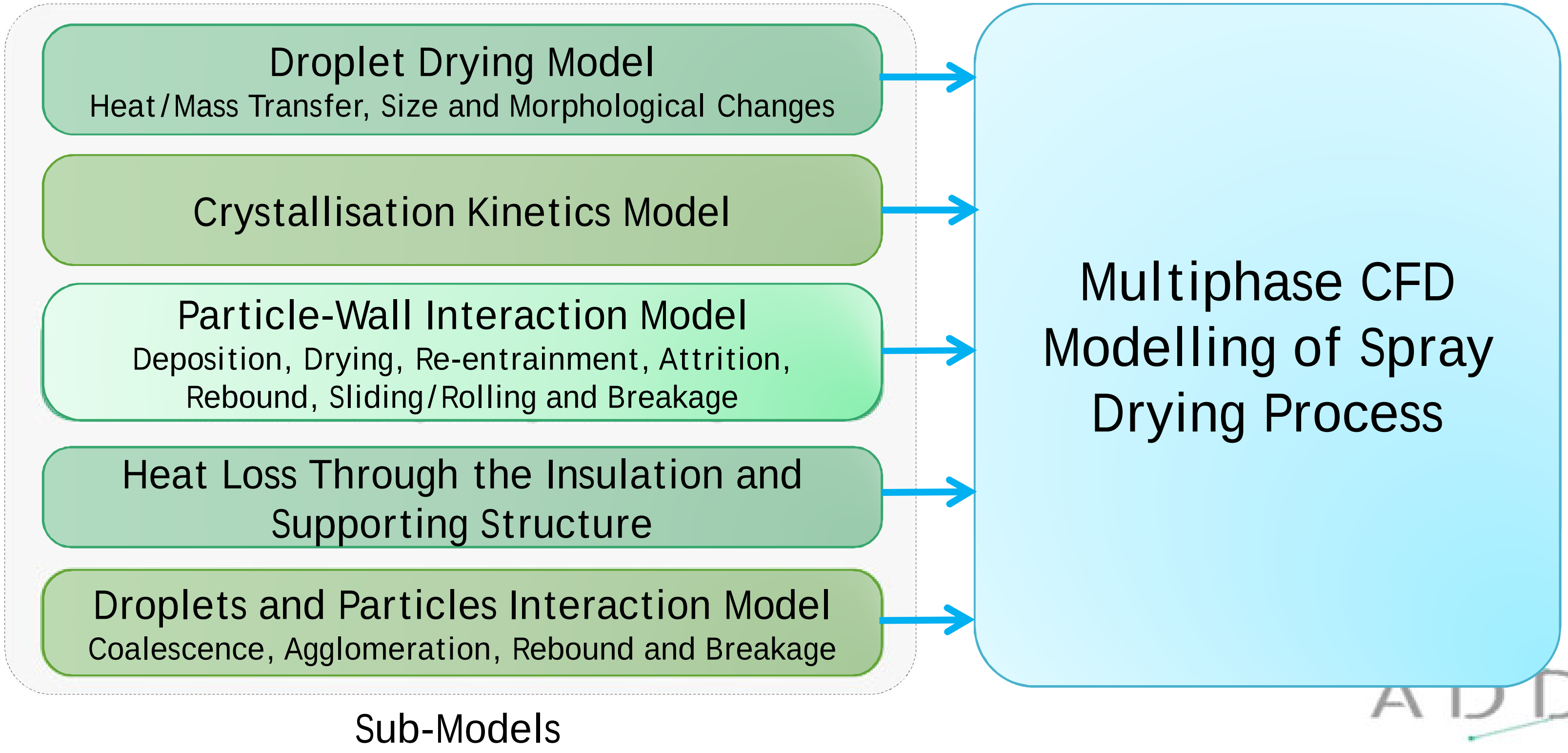
Time-Averaged Air Flow Profile



Contours of LES predicted air flow profiles coloured by velocity magnitude

Spray Drying Modelling

- ➢ Spray drying towers involve complex, 3-D turbulent gas flow
- ➢ Modelling of gas flow is critical to successful prediction
- ➢ Computational Fluid Dynamics (CFD) modelling is the preferred choice



Droplet Drying Model
Heat/Mass Transfer, Size and Morphological Changes

Crystallisation Kinetics Model

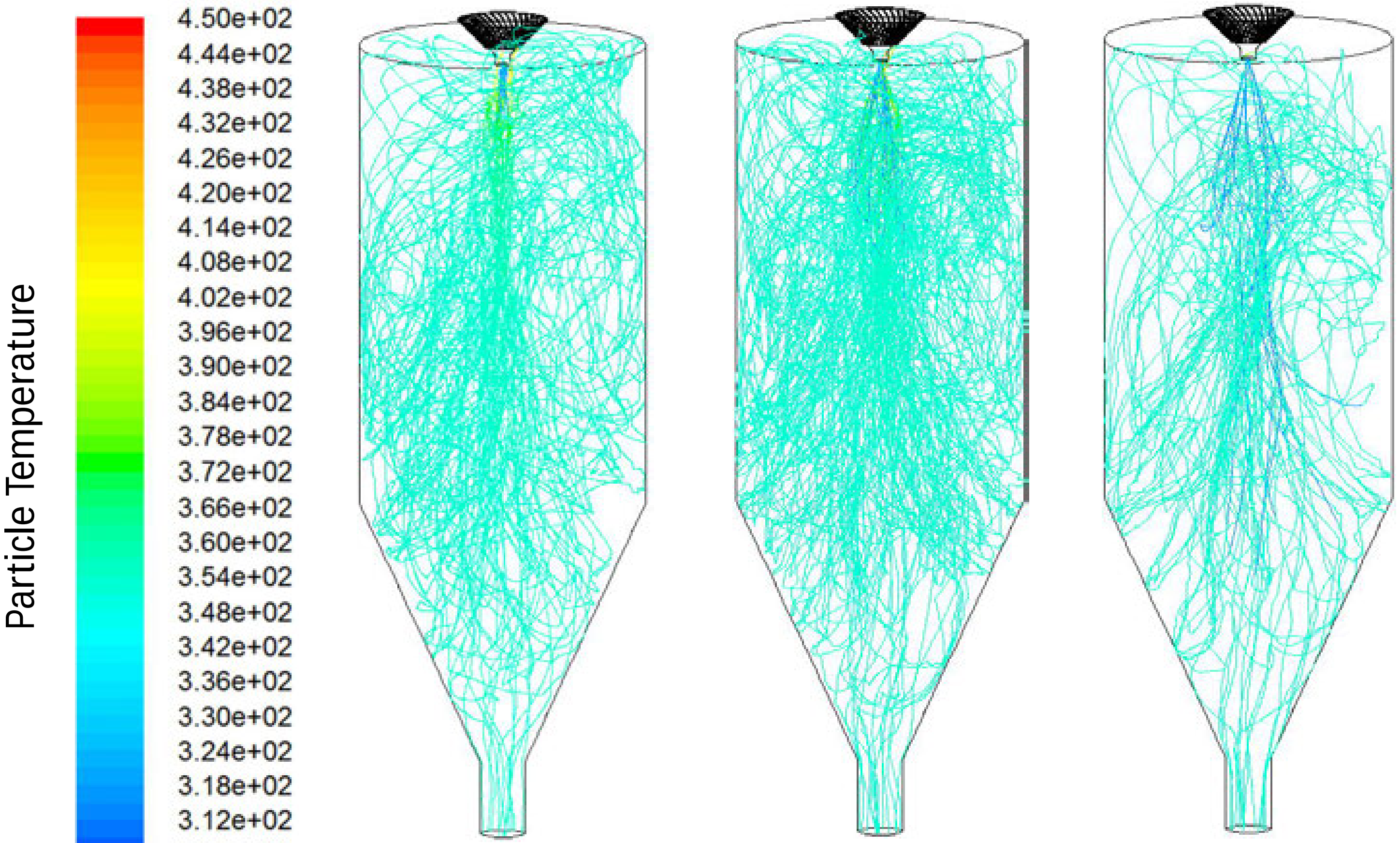
Particle-Wall Interaction Model
Deposition, Drying, Re-entrainment, Attrition, Rebound, Sliding/Rolling and Breakage

Heat Loss Through the Insulation and Supporting Structure

Droplets and Particles Interaction Model
Coalescence, Agglomeration, Rebound and Breakage

Sub-Models

Multiphase CFD Modelling of Spray Drying Process

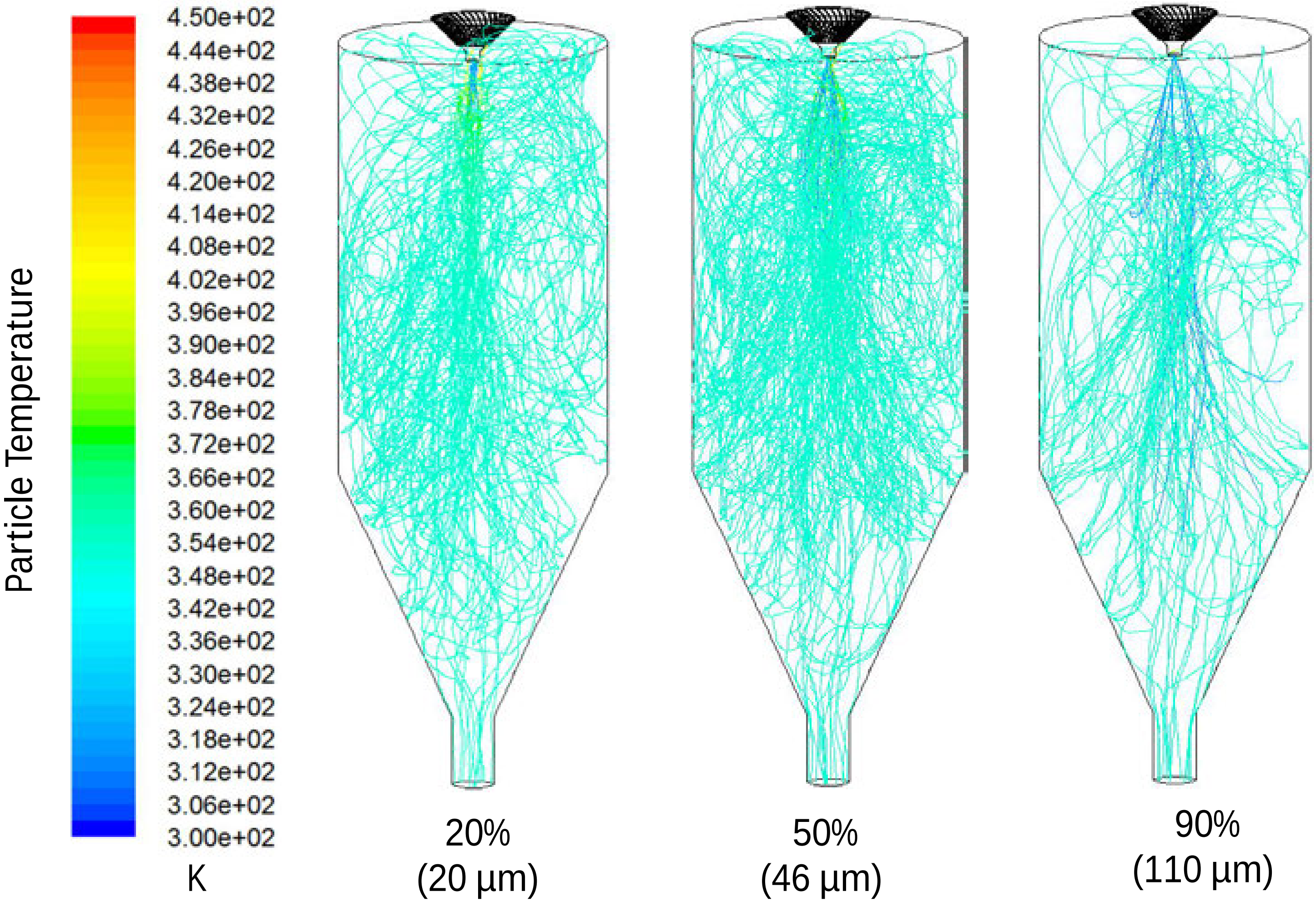


20%
(20 µm)

50%
(46 µm)

90%
(110 µm)

Trajectories coloured by Particle Temperature

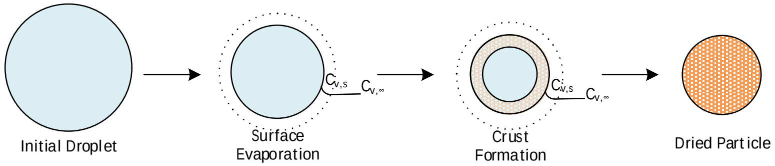


20% (20 µm)

50% (46 µm)

90% (110 µm)

Improving Drying Models

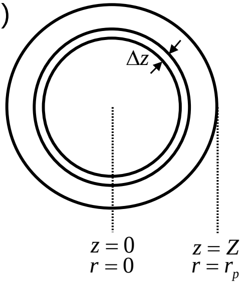


- Historically simplified models have been used in CFD
- What impact does this have?
- Compare simplified approaches (CDC and REA) with full solution of diffusion equation

- Diffusive transport equation in solute fixed coordinate system

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial z}\left(D(u,T) C_s^2 r(t)^4 \frac{\partial u}{\partial z} \right) \qquad (1)$$

$$\partial z = C_s\, r(t)^2\, \partial r \qquad (2)$$



Initial condition ($t \le 0$):

$$u = u_{initial} \qquad 0 \le z \le Z \qquad (3)$$

Boundary conditions ($t > 0$):

$$\left.\frac{\partial u}{\partial z}\right|_{z=0} = 0 \qquad (4)$$

$$-D(u,T) C_s{}^2 r_p{}^2 \left(\left.\frac{\partial u}{\partial z}\right|_{z=Z} \right) = k(a_w\, C_{v,s} - C_{v,\infty}) = \frac{\partial M_l}{\partial t} \Big/ A_{drop} \qquad (5)$$

where

D is solvent diffusivity

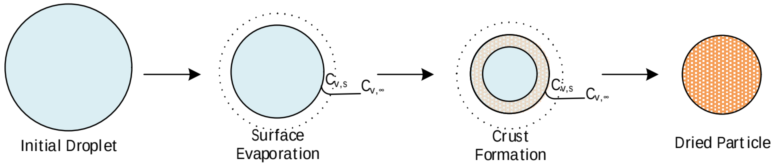
C_s is solute concentration

C_v is vapour concentration

k is mass transfer coefficient

u is solvent mass fraction

Improving Drying Models



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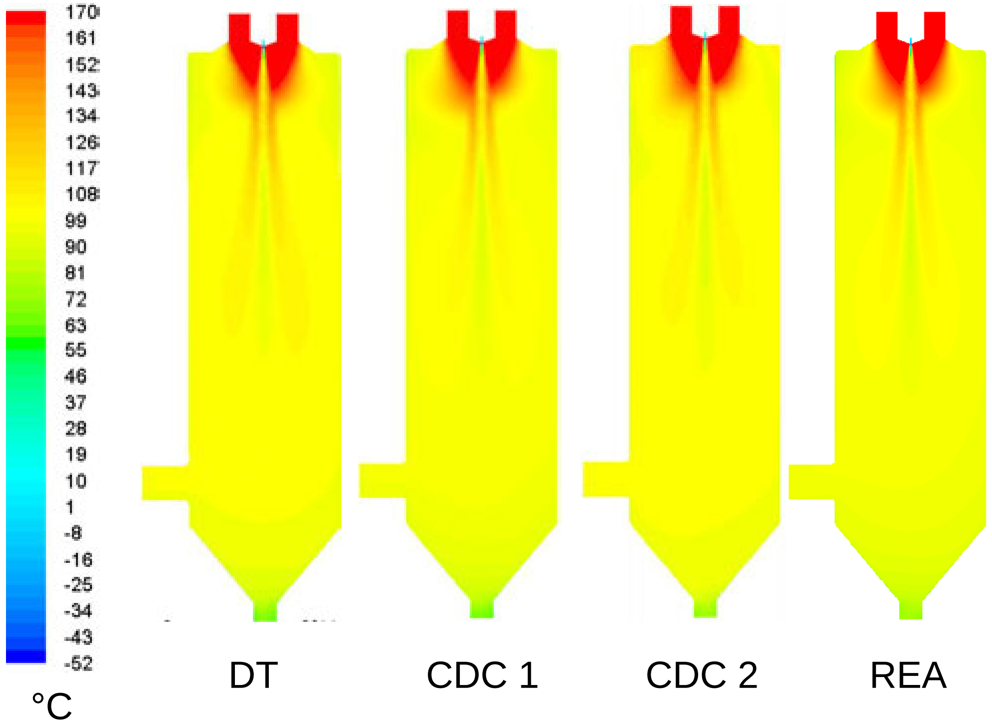

Moisture Profile and Yield

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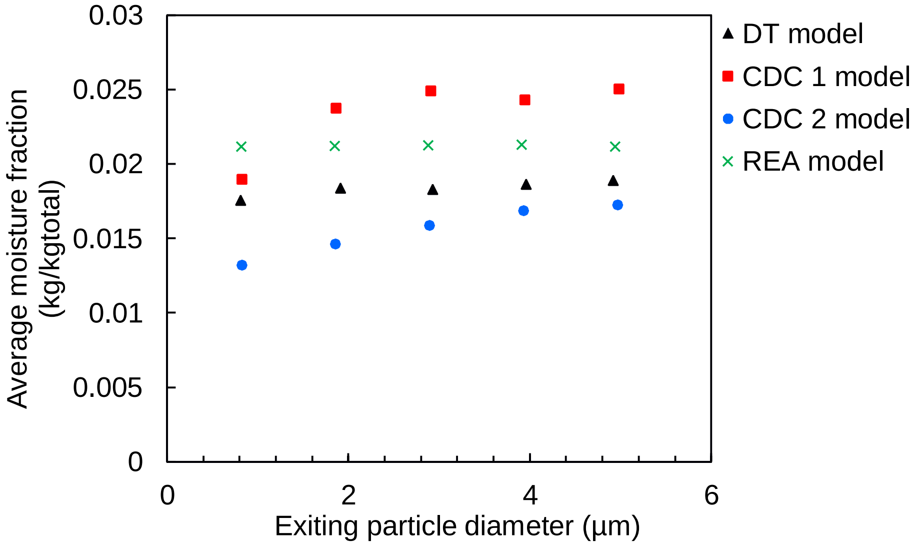

Average moisture fraction of exiting particles

Model	Yield
DT	48%
CDC 1	19%
CDC 2	60%
REA	25%
Measured[1]	47%

Dried powder yield predicted using different drying models

- SIGNIFICANT DIFFERENCE BETWEEN DIFFUSION BASED MODEL AND SIMPLIFICATIONS
- IMPROVED VERSION OF CDC SHOWS POTENTIAL

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1. Islam and Langrish (2010). Food Research International, vol. 43, pp. 46-56.

Summary

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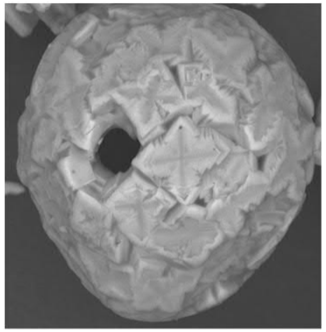
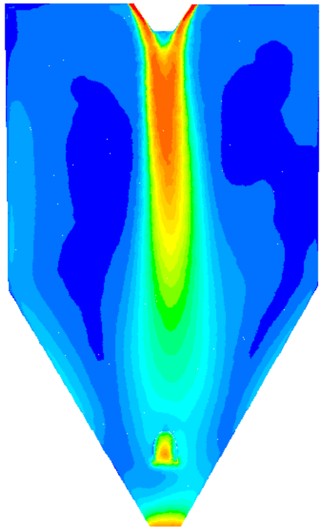
- *Single Droplet:* single particle methods developed give insights into solidification and structure formation mechanisms
- *Droplet Interactions*: Extended understanding of collision behavior on simplified and real systems, new models
- *Process:* Improvements to spray drying models – bringing structure effects into the drying models





a.e.bayly@leeds.ac.uk

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Thank you.

Questions?