Crystallisation-Induced Flows in Evaporating Aqueous Saline Drops

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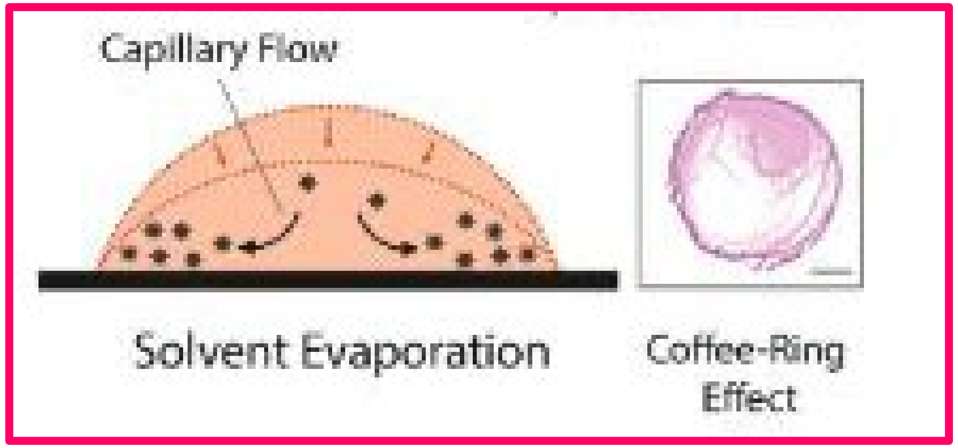
Coffee – Ring Effect

'Coffee –ring' Effect: Initially reported by Deegan in 1997 [1] for coffee droplets. A 'ring deposit' is formed when the contact line is pinned during evaporation, because of a capillary flow that transfers material from the centre of the droplet to its edges, where it is accumulated. This also applies in drops containing other suspensions or soluble solids.



[2] S. W. Song, H. J. Bae, S. Kim, D.Y. Oh, O. Kim, Y. Jeong, and S. Kwon, Part. Part. Syst. Charact. **34**, 1 (2017)

The first stage to the investigation of more complex fluids such as salt – protein mixtures

Drying of Saline Droplets

Pharmaceutical Applications

Weathering Processes

Medical Diagnostics

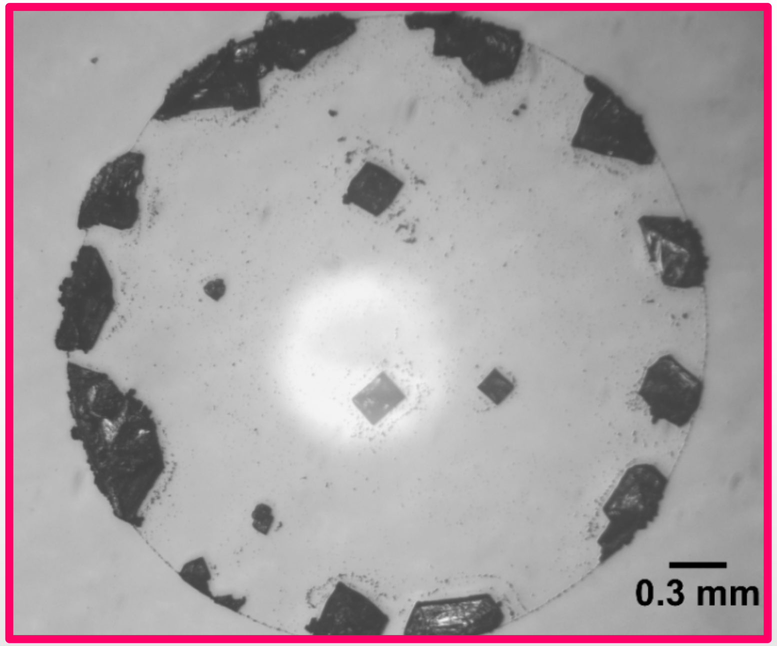
[1] R. D. Deegan, O. Bakajin, and T. F. Dupont, Nature **389**, 827 (1997)

Experimental Methodology

No study on the investigation of **internally induced flows during nucleation and crystallisation.**

Our work:

- Experiments on micro-litre drops of saline solution (1M), evaporating on hydrophilic glass slides with a low initial contact angle.
- To examine **WHY** instead of obtaining a complete crystal ring, a **ring of roughly evenly spaced crystals is observed for aqueous saline droplets**.

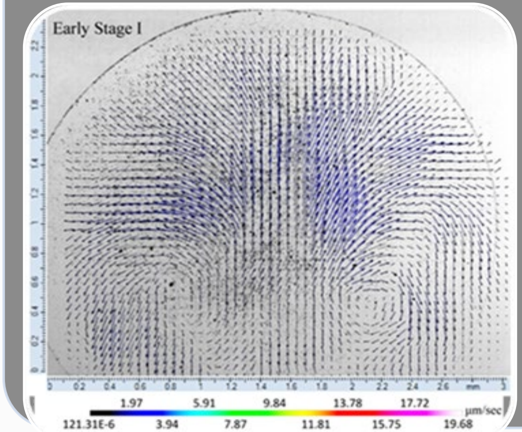


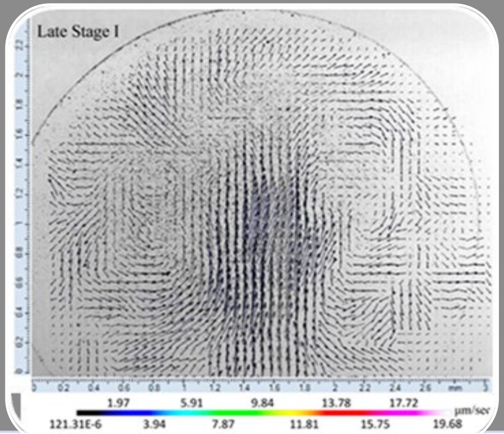
Micro – PIV (Particle Image Velocimetry): for the visualisation of the flow at the flat base of the droplets (to avoid optical distortions caused by the curvature of their upper surface)

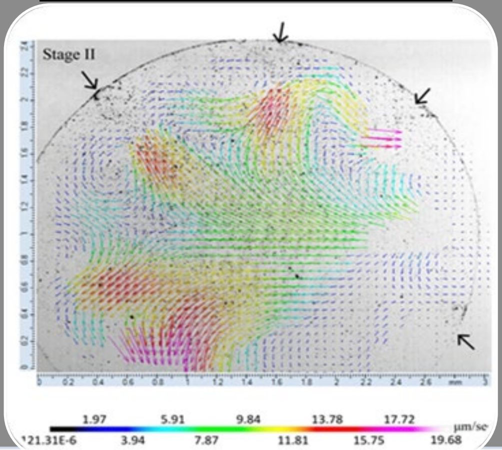
Results

Stage I

Stage II







Early part

Initial **slow generally outward flow** at the bottom layer of the droplet, carrying fluid towards the contact line.

Latter part

The outward flow at the base slows by an order of magnitude immediately prior to the nucleation of the first crystal near the periphery of the droplet

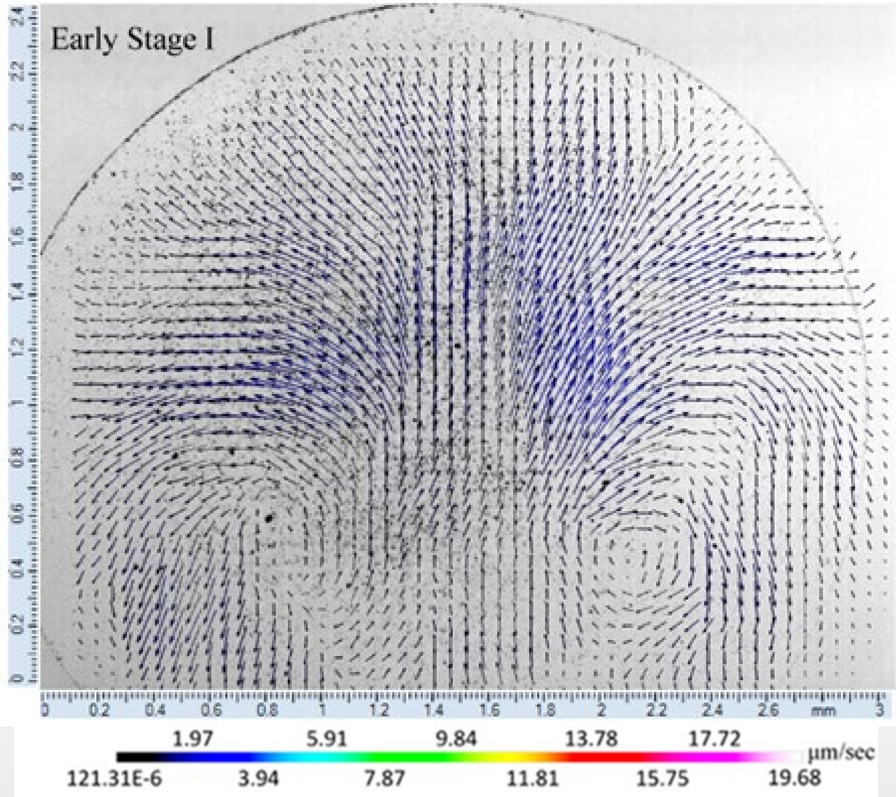
Strong jet-like flow towards the point where the first **crystal** is formed (Fluid velocity dramatically increased towards the crystal: Vmax ~20µm/sec)

Formation of vortices as the jet displaces fluid out along the contact line.

0-60% | 60-70% | 70-100% | tfinal

Results

Early Stage I: Generally outward flow
(not perfectly radially outwards due to Marangoni convection)



Calculated Velocity required to supply the evaporative flux – Continuity
based on the CA, droplet height, volumetric flow rate, concentration difference within the droplet
~6 µm/sec

Velocities measured from micro-PIV: 1-3 µm/sec

- Lower value for the measured flow: consistent with the presence of a solutal Marangoni driven convection at the surface

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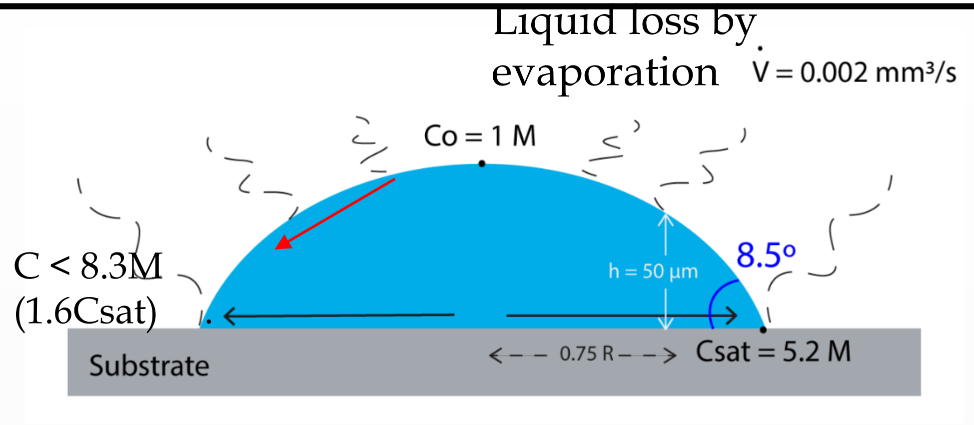

$$h(r,t) = \sqrt{\frac{R^2}{\sin^2\theta} - r^2} - \frac{R}{\tan\theta}$$

R: full radius of the droplet
θ: contact angle
r: 75% of the droplet radius

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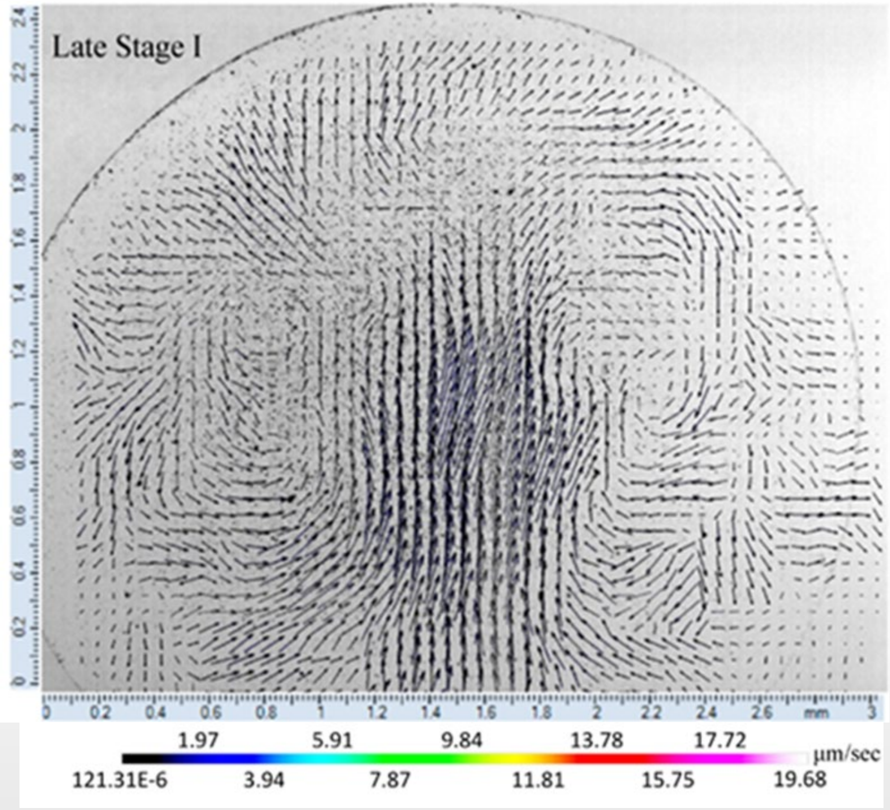
Results

Late Stage I

The velocities near the base of the droplet decrease significantly, just before crystallisation occurs.



Assumptions:

- The drop is at the point of incipient nucleation near the contact line (concentration at the CL: 1.6 Csat [5])
- Concentration near the apex: Co
- Volumetric flow rate: almost constant during this stage
- Marangoni-driven convective flow at the air – liquid interface sufficient to supply almost all of the evaporative flux, causing the flow at the base to decrease to almost zero

Estimated depth of the surface flow region: ~0.6 µm at 75% of the radius
Convective velocity at the air – liquid interface: of the order of hundreds of µm/sec

[5] J. Desarnaud, H. Derluyn, J. Carmeliet, D. Bonn, and N. Shahidzadeh, J. Phys. Chem. Lett. **5**, 890 (2014)

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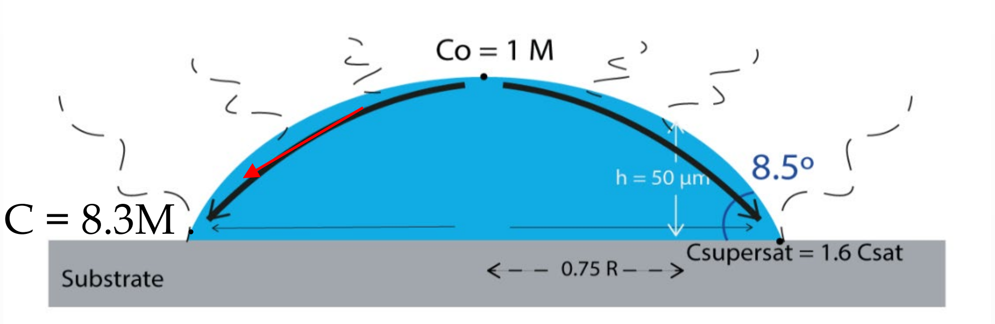
Same evaporation rate



Shear Stress Equation

$$\upsilon = \frac{1}{\eta}\left(\frac{\partial\gamma}{\partial c}\right)\frac{\Delta ch}{l}$$

η: fluid viscosity

$\left(\frac{\partial\gamma}{\partial c}\right)$: change in the surface tension based on the salt concentration

Δc: salt concentration difference

h: thickness of the film

l: the film width

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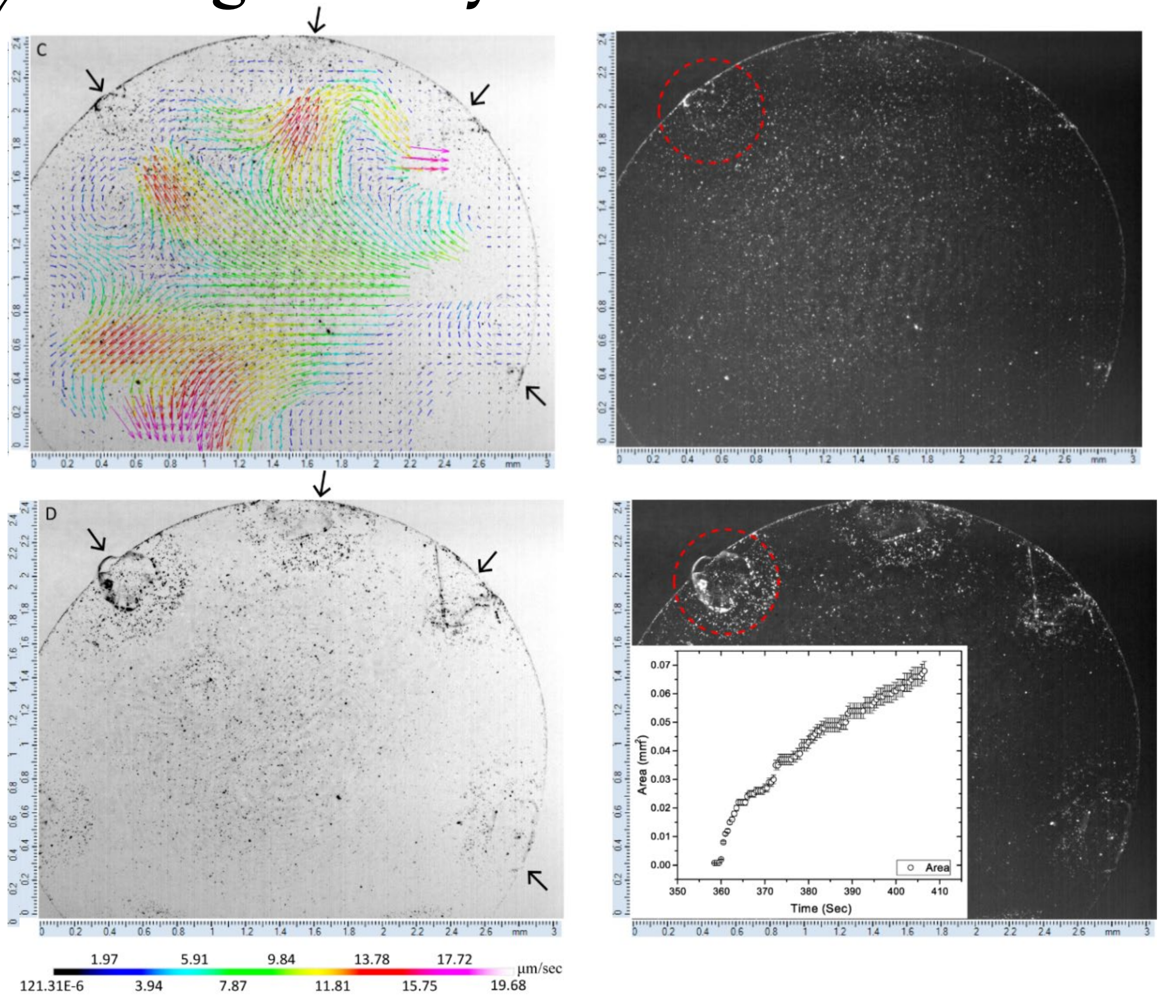
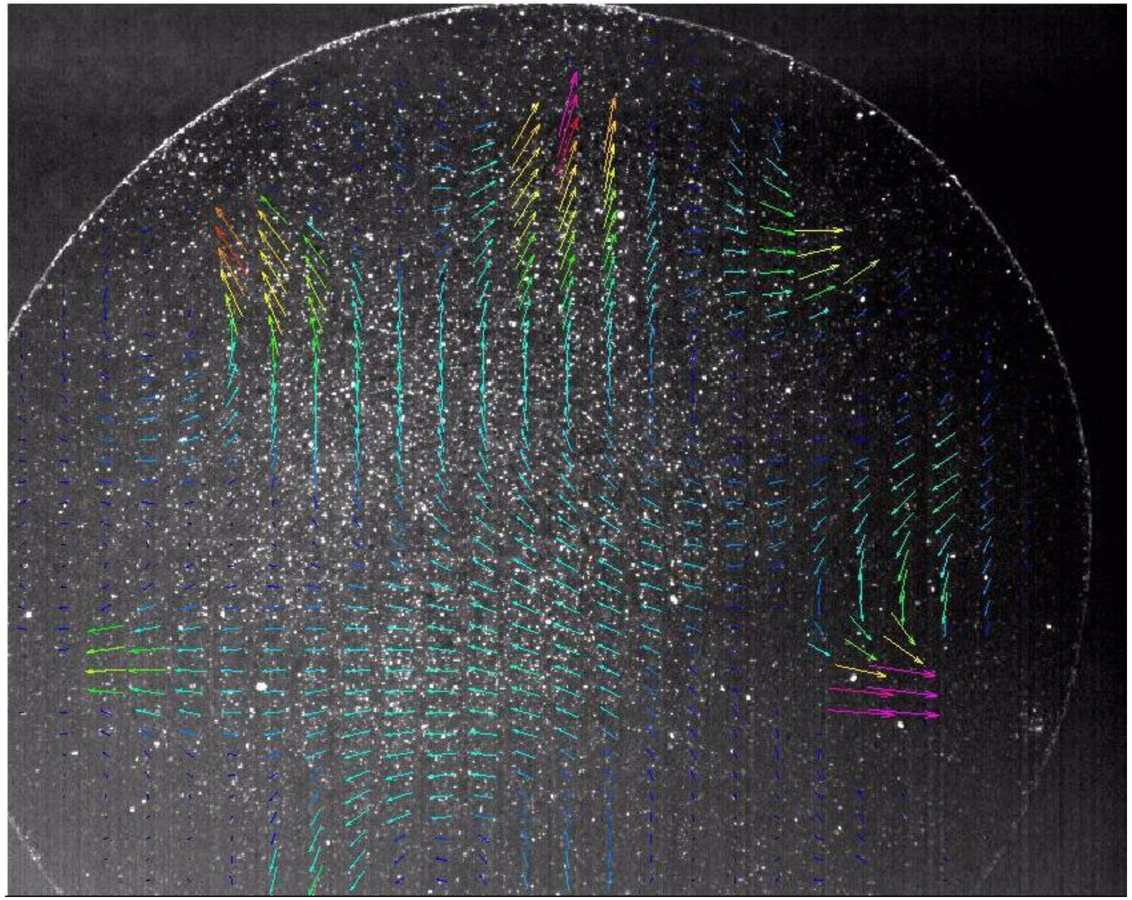
Stage II : Crystallisation-driven Flow





Results

Stage II : Crystallisation-driven Flow

- Nucleation occurs and crystals start to grow near the contact line. Both nucleation and crystal growth are associated with a jet of fluid.

- Concentration: expected to drop from its supersaturated state towards saturation in the immediate vicinity of the crystal.

- The concentration-based surface tension driving force is reduced by ~40%

- Hence, the radially outward surface flow is reduced locally (by approximately 40%)

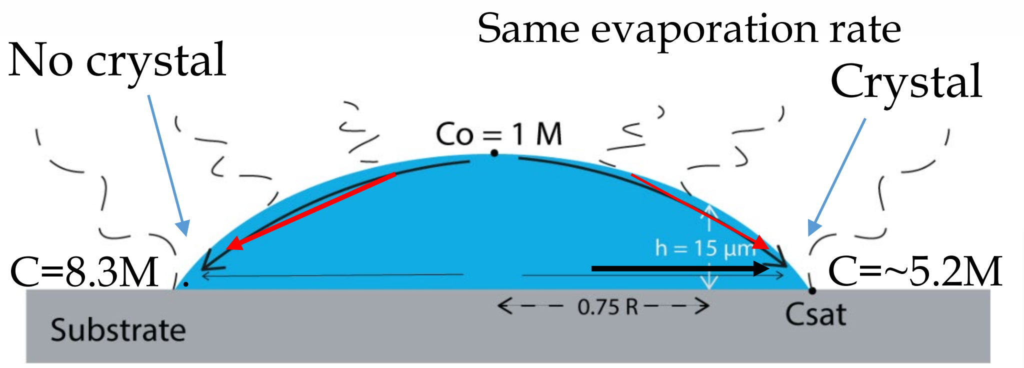
Results

Stage II : Crystallisation-driven Flow

Assumption:
Thickness of the surface layer over which the surface tension force has an effect: same as for that in the later part of stage I

Volumetric Flow rate decreases

- outward flow in the lower region of the drop to meet the required evaporative flow (unchanged by crystallisation)



$$h(r,t) = \sqrt{\frac{R^2}{sin^2\theta} - r^2} - \frac{R}{tan\theta}$$

R: full radius of the droplet
θ: contact angle
r: 75% of the droplet radius

Calculated lower layer velocity required : 9 µm/sec
Velocities measured in experiments for the jet towards the crystal: ~14 µm/sec

Stage II : Crystallisation-driven Flow

Jet-like flow entrains surrounding fluid

↓

Formation of counter-rotating **vortices** along the base of the drop. Within the vortices, the fluid concentration is reduced due to salt crystallisation.

- The vortices create a zone close to a growing crystal where further nucleation is less likely.

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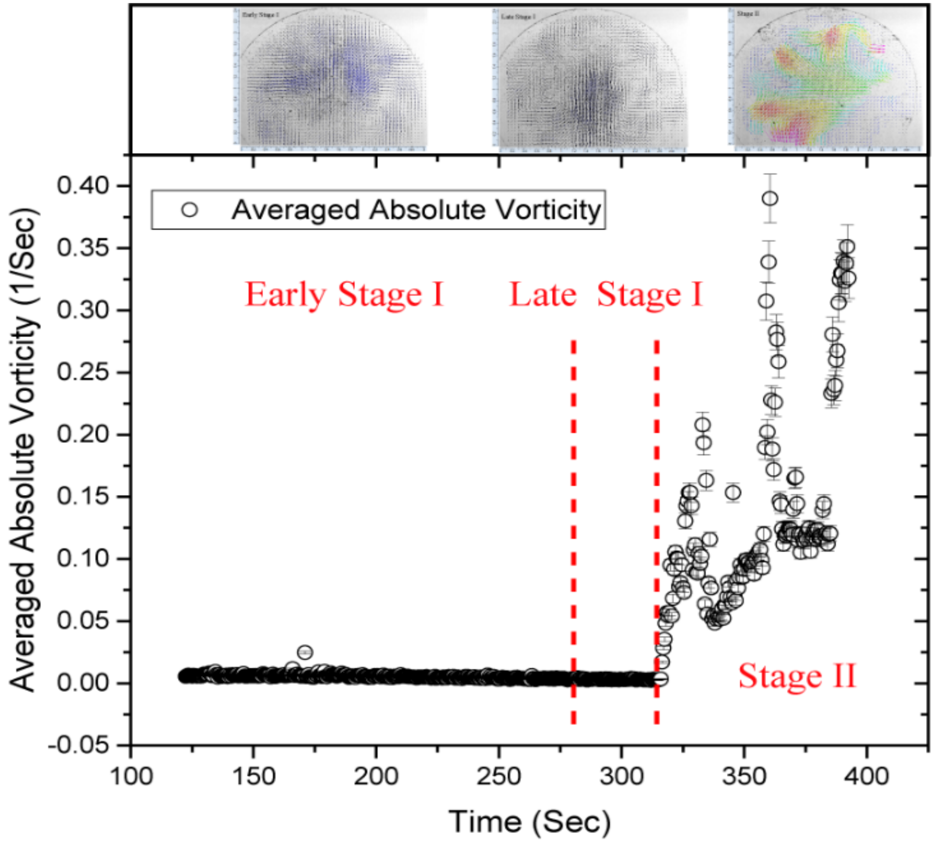
This justifies why the deposits form a sequence of crystals around the periphery of the drop rather than a continuous ring.



Concluding Remarks

- Correlation between flow and crystallisation of aqueous saline droplets of relatively high salt concentration on hydrophilic glass slides

- Existence of two stages during evaporation

  I. Generally outward flow, followed by a momentary pause of the flow, when the velocity is reduced by orders of magnitude.
  II. Jet – like flows towards the growing crystals and increasing vorticity in the droplet
     - **Crystal nucleation has a direct effect on the flow regime**

Further Questions

- Will this 1-D analysis be borne out by full 3-D flow analysis?
- Is this flow dependent on the degree of supersaturation required for nucleation?
- How does temperature of substrate affect the internal flows?

Thank you