Behavior of a Salt Water Solution Near the Critical Point Under Microgravity Conditions

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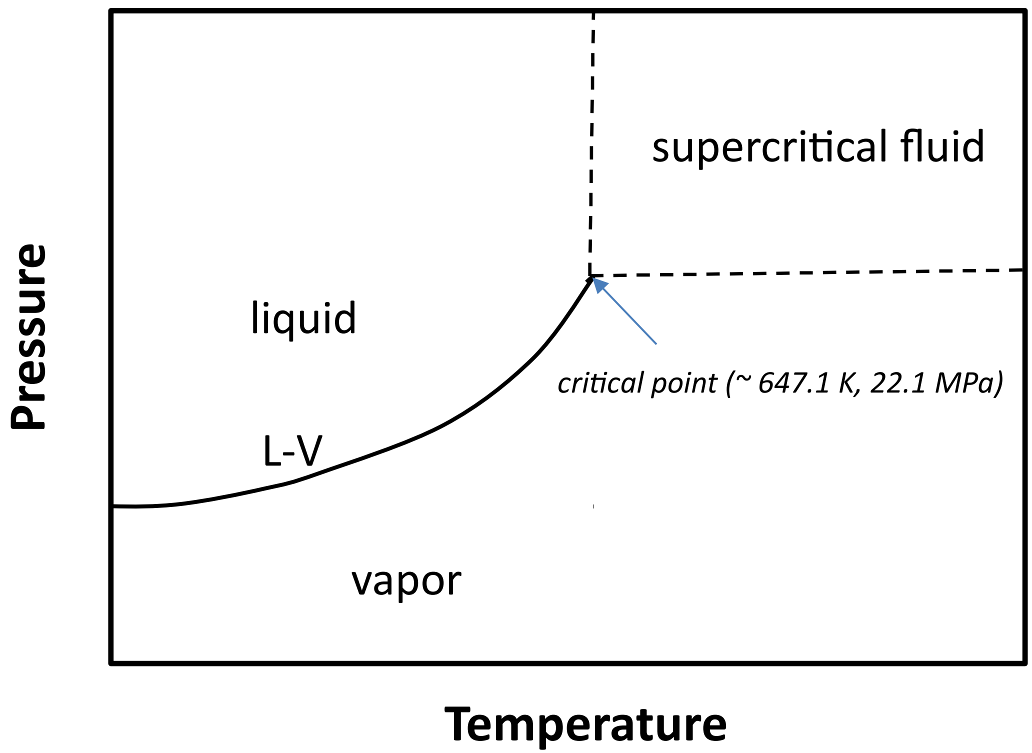
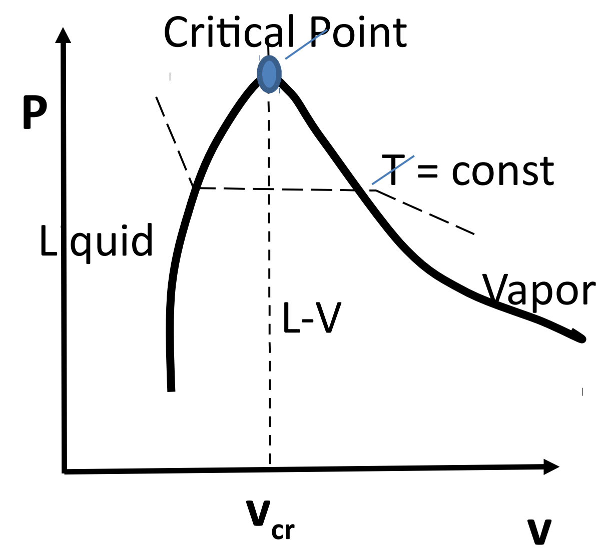
Supercritical Water Phase Diagram



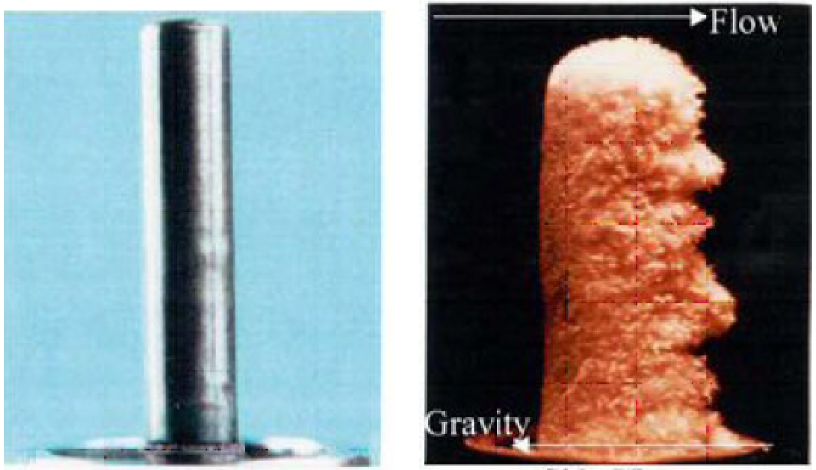


- Singular behavior near the critical point (highly compressible, thermal diffusivity →0)
- Fundamental and practical interest- ***water reclamation*** and ***waste management*** technologies (organic compounds, gases highly soluble in supercritical water)

Why Supercritical Salt Water Mixtures?

- Spacecraft waste streams either contain various salts or they may occur during neutralization of acids formed during oxidation
  - sodium carbonate used for neutralization of HCl
  - sodium sulfate formed during neutralization of sulfuric acid

Na_2SO_4 at 4 wt % , T_B = 356°C, P = 250 atm



Before Run **Side View**

Figure[1] shows the rapid deposition on a heated surface inserted into a flowing water/salt solution and maintained at a temperature just above that of the solubility limit in the bulk fluid

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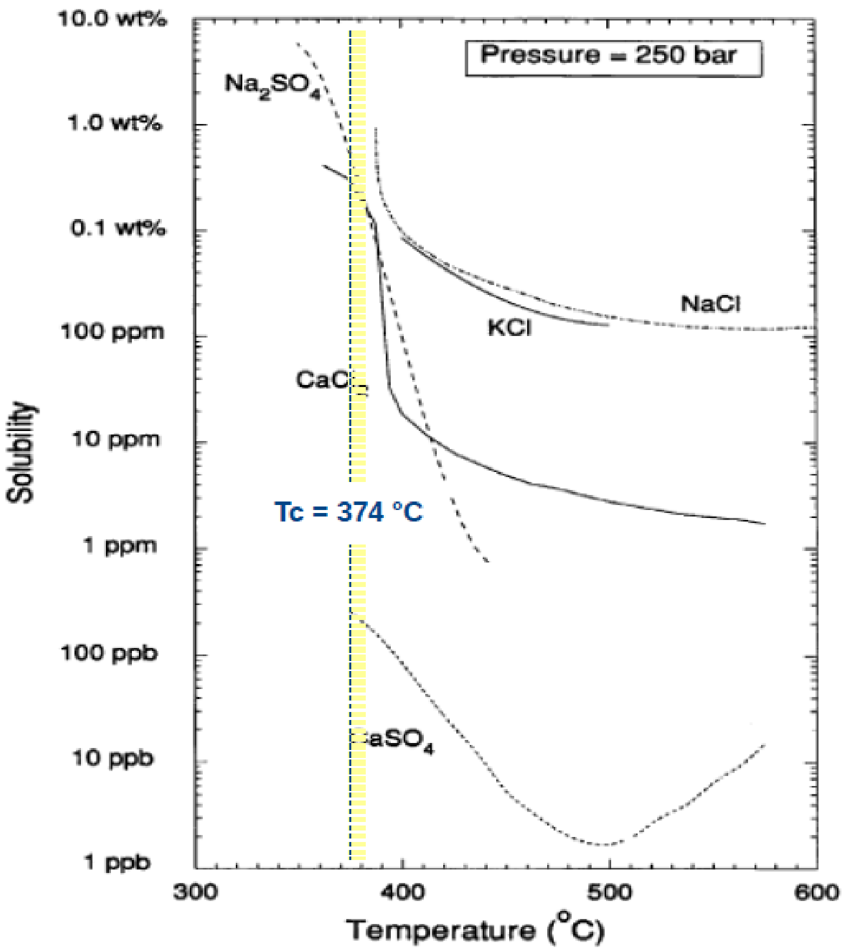
[1] *Hodes, M., Marrone, P., Hong, G.T., Smith, K. A., Tester, J. W., Salt precipitation and scale control in supercritical water oxidation - Part A: fundamentals and research; Journal of Supercritical Fluids; 29 (2004) 265–288*

Salt Solubility and Precipitation



- Many salts of interest start precipitating at low concentrations near the critical transition conditions

  $\ln(x) \sim A + B \ln(\rho)$

- How does presence of salt effect liquid-vapor phase distribution in microgravity?
- Where does the salt precipitate?
- How much does critical temperature change with addition of salt?

Objectives

- Overall Objective

  Investigate the behavior of an isochoric salt-water mixture near its critical point under microgravity conditions

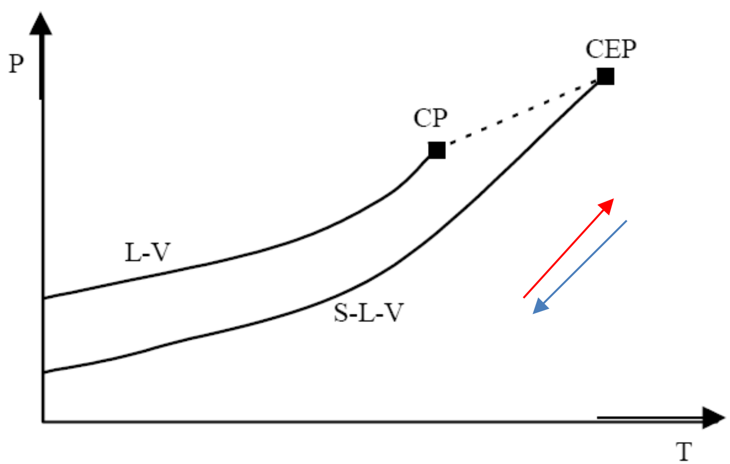
- Specific Objectives
  - Investigate the phase distribution as critical transition is approached

    partitioning of fluid into liquid and vapor phases

    partitioning of salt between liquid and vapor
  - Determine shift in the critical temperature compared to critical water
  - Investigate precipitation behavior

Experimental Method

- Closed test cell filled with salt water solution (0.5% w Na_2SO_4) at close to critical density of water (322 kg/m3)
- Heat or cool test cell at programmable rates :
  - 0.5 mK/min to 10 mK/sec for heating
  - 0.5 mK/min to 5 mK/sec for cooling



- Ideally reversible phenomena during heating/cooling
- Two factors prevented ideal reversibility:
  - salt precipitation on windows that does not fully redissolve
  - formation of denser phase fluid

    Heating rate limitations?

"Solubility of Sodium Sulphate in the Vicinity of the Critical Point", Daucik, K, and Jensen, J. P., 14th International Conference on the Properties of Water and Steam, Kyoto, 2004.

DECLIC Facility on ISS

Experiment Locker (EXL) houses the optical bench, light sources and sensors (3 cameras, 2 photodiodes, 3 accelerometers)

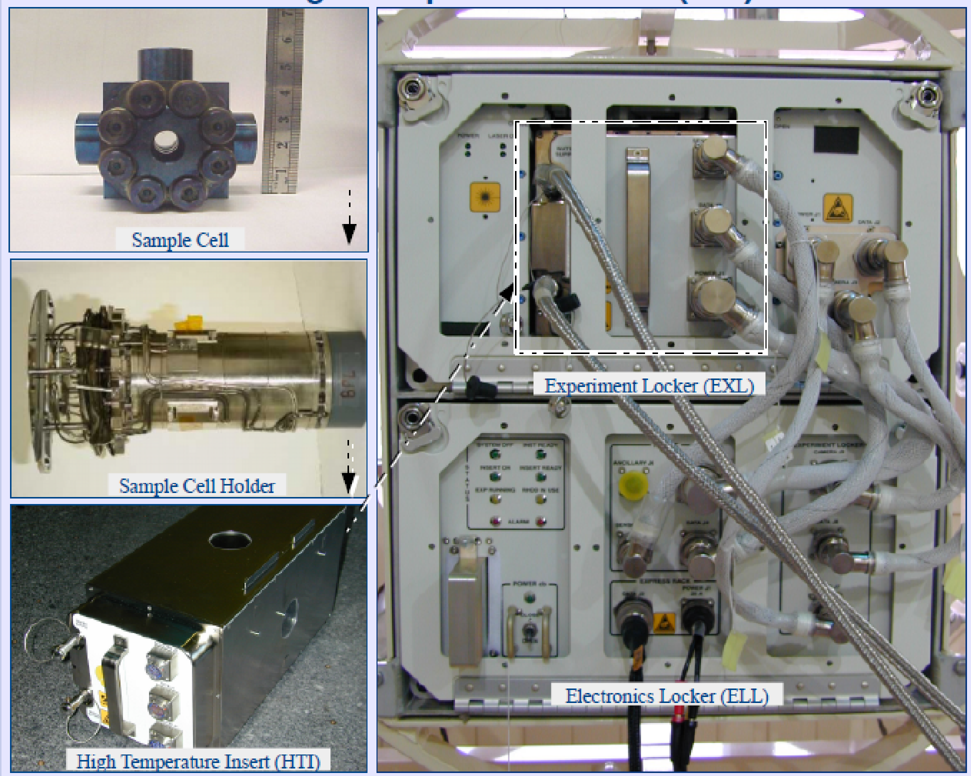
Electronic locker (ELL) includes the power and data handling, and thermal regulation

HTI Insert contains the fluid cell and the dedicated conditioning hardware

- **Insert Size:** 200x200x450 mm^3
- **Test Cell:** aqueous solution of Na_2SO_4 at 0.5%-w at critical density (0.322 g/cm^3)
- **Fluid Volume:** 0.3 mm^3 coin shaped

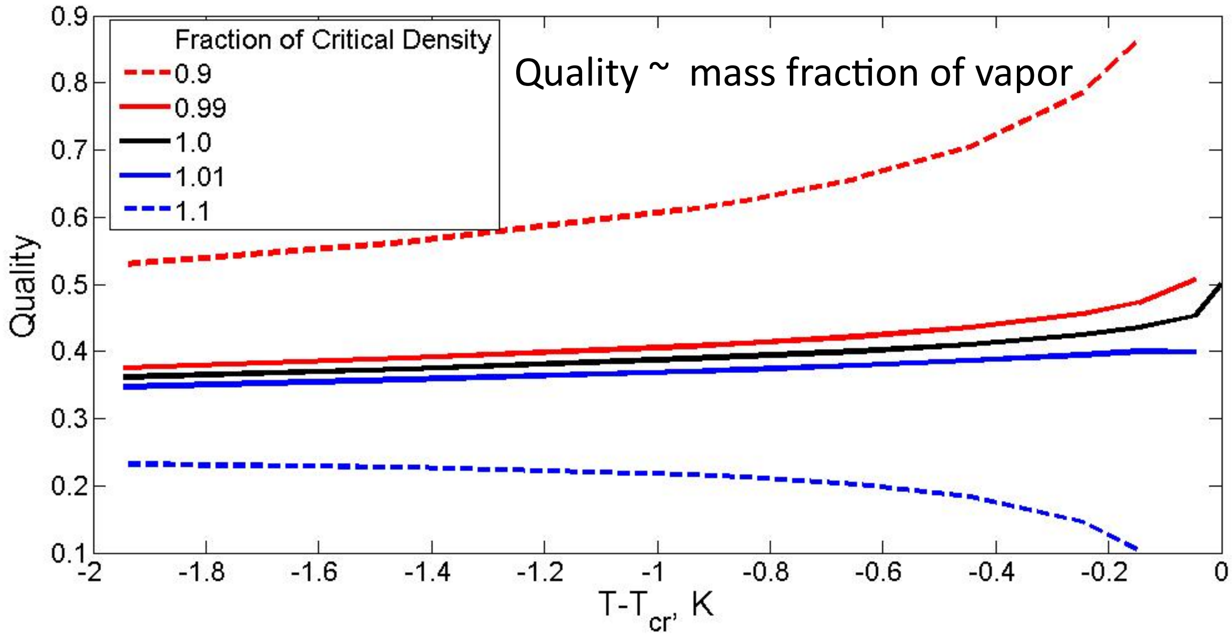
Diagnostics: temperature measurements (3 cell sensors), turbidity measurement, video imaging (2 primary cameras … Wide and Small FOV)

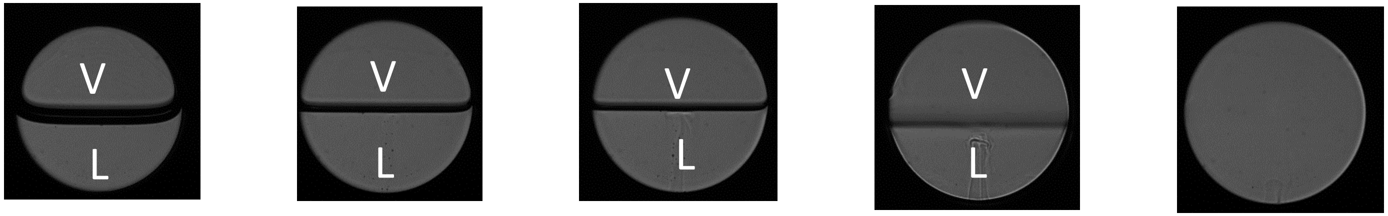
DECLIC Facility
w/ High Temperature Insert (HTI)



- Temperature Regulation : 350°C to 455°C
- Max rate: heating 10 mK/s, cooling 5 mK/s
- Accuracy: 40 mK with calibration
- Reproducibility: ±10 mK
- Stability: better than ± 1 mK/h
- Quench: ±1 to ±300 mK
- Gradient over fluid cell < 1 mK/cm

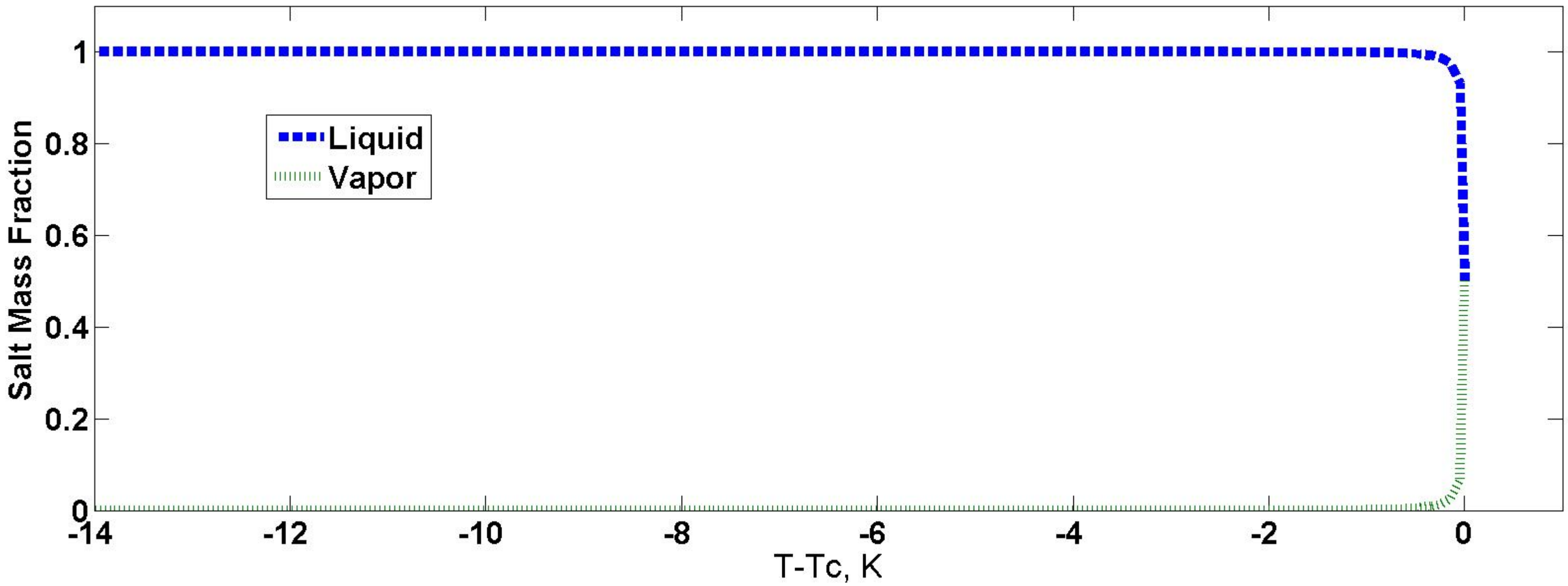
Estimate of Quality (liquid-vapor partitioning) vs Temperature





- Estimate based upon pure water properties (NIST database)
- If cell is filled at the critical density there should be equal mass of vapor and liquid just below the critical temperature since liquid and vapor densities become equal.

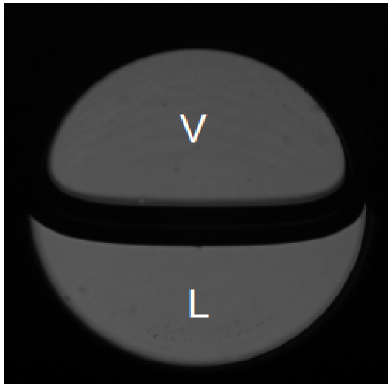
Estimate of Salt Partitioning vs Temperature



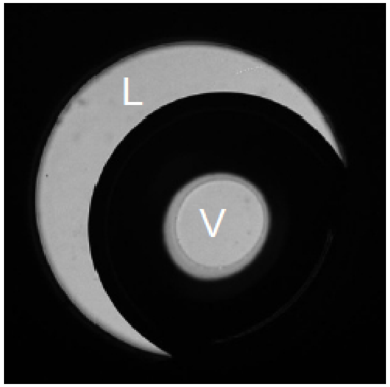
- $\ln (x_v/x_l) = -(4805/T) \ln (\rho_l/\rho_v)$
  Shvedov and Tremaine, J. Sol. Chem., 29, 10, 2000.

- Unprecipitated salt stays mainly in the liquid phase until close to critical conditions.

Phase Distribution Below the Critical Point
T = 351 C
Pure Water



1-g



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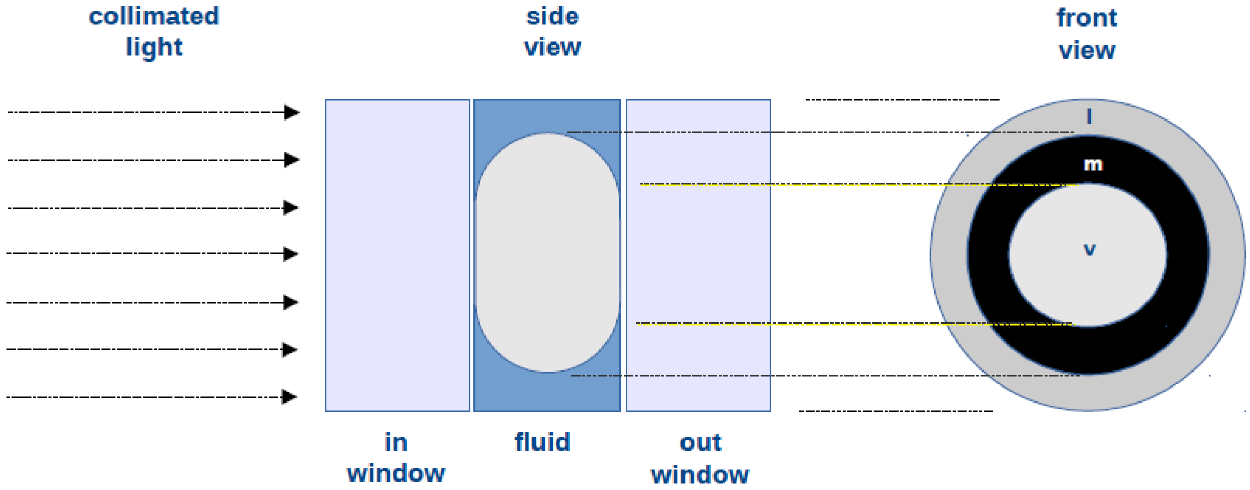
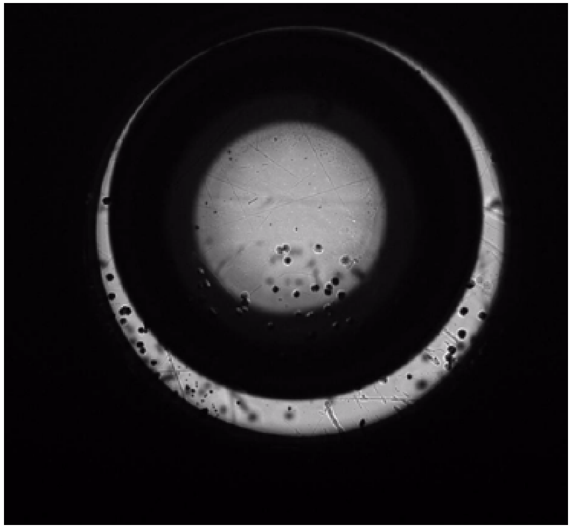
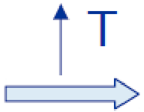
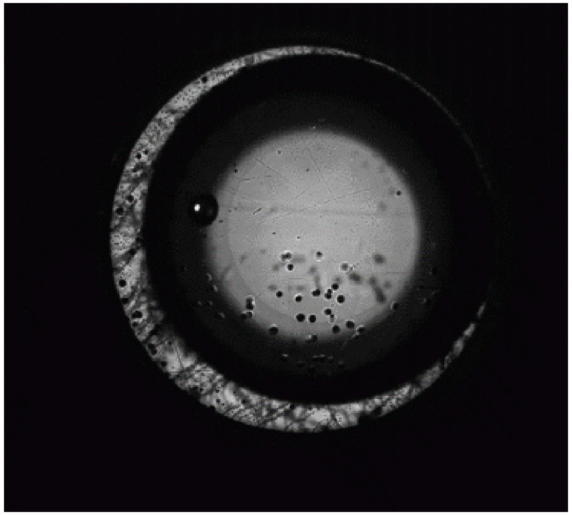


Incipient Boiling ~ 373 C



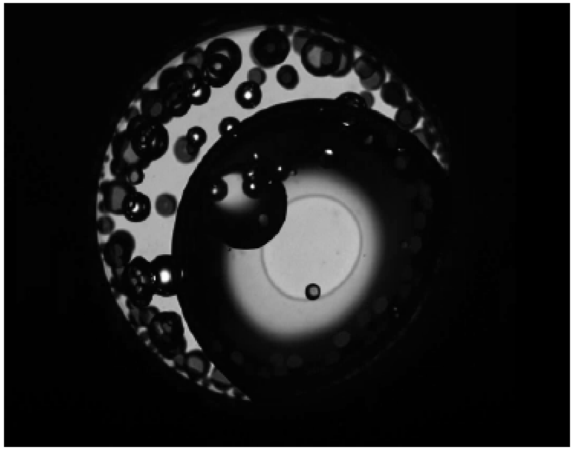


Incipient boiling becomes more vigorous



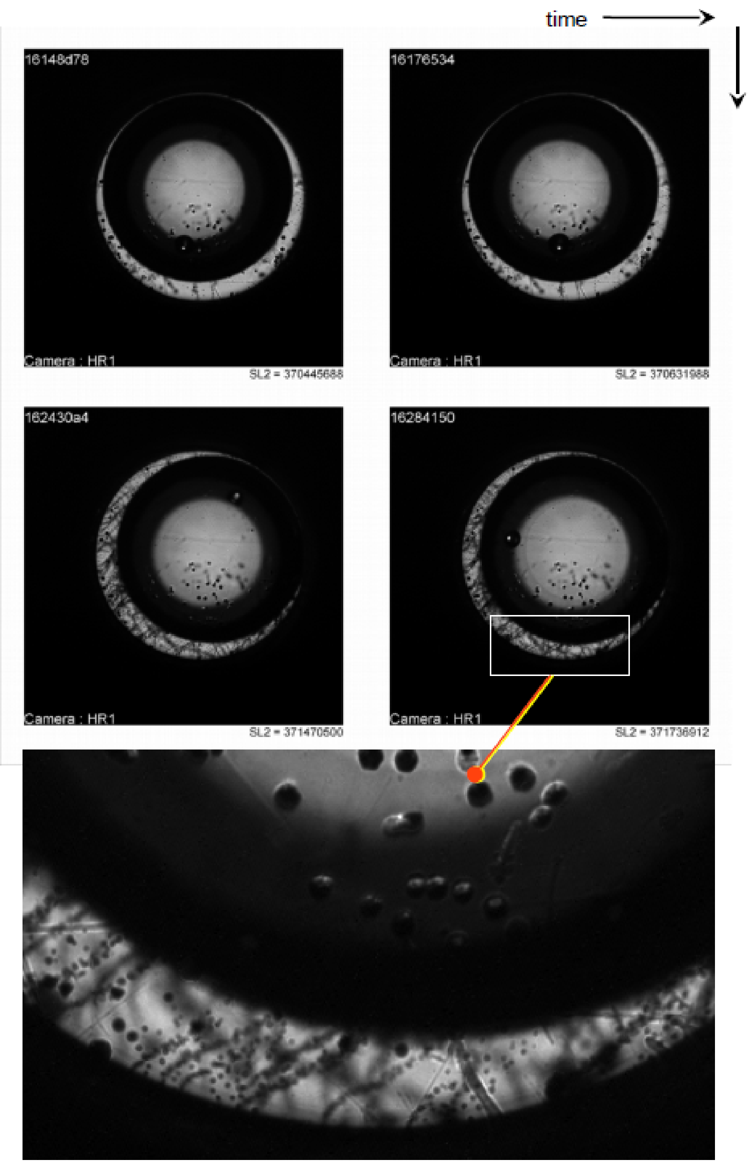
- Bubble size ~ 20 microns
- Smaller and less disperse bubbles compared with pure water

Boiling in pure water ~ (Tc – 2K) →



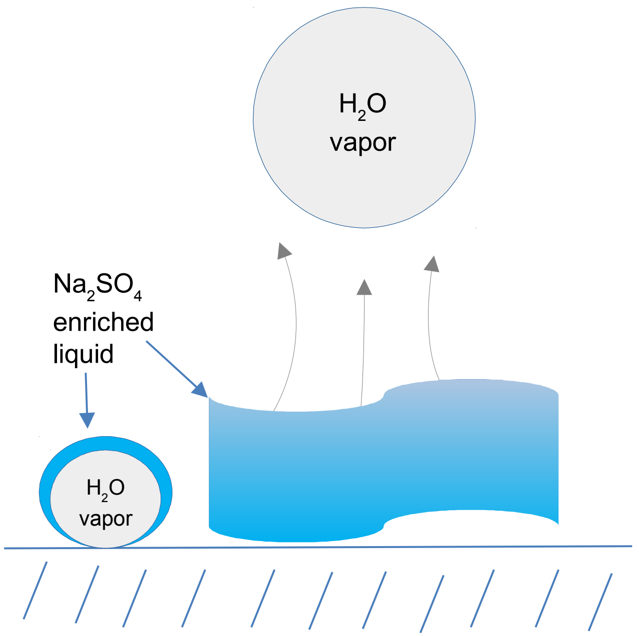
Channeling of Vapor Bubbles

- Bubbles form discrete channels as they move to the L-V interface
  - Wake effect of preceding bubble
  - Localized salinity gradients
- Channels less discernible as bubbling becomes more intense



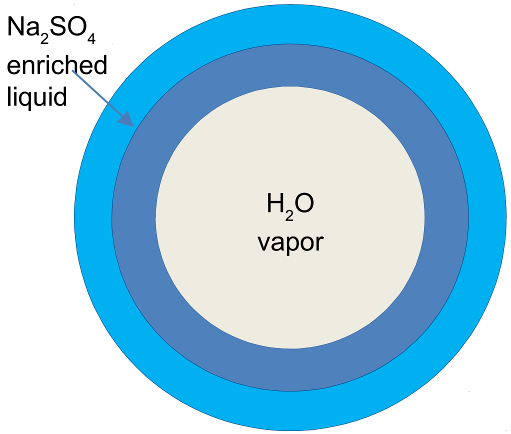
Formation of Salinity Gradient Near the Wall

- Below the critical temperature salt partitions favorably into the liquid
- Vapor bubbles generated at the wall are effectively pure H_2O.. leaving a localized liquid region around the vapor bubble at higher Na_2SO_4 concentration
- As vapor generation intensifies this leaves a higher salinity and higher density liquid near the walls



Formation of Salinity Gradient Near the Central Vapor Bubble

- Below the critical temperature salt partitions favorably into the liquid
- During the liquid-vapor interchange process salt stays in the liquid near the liquid-vapor surface



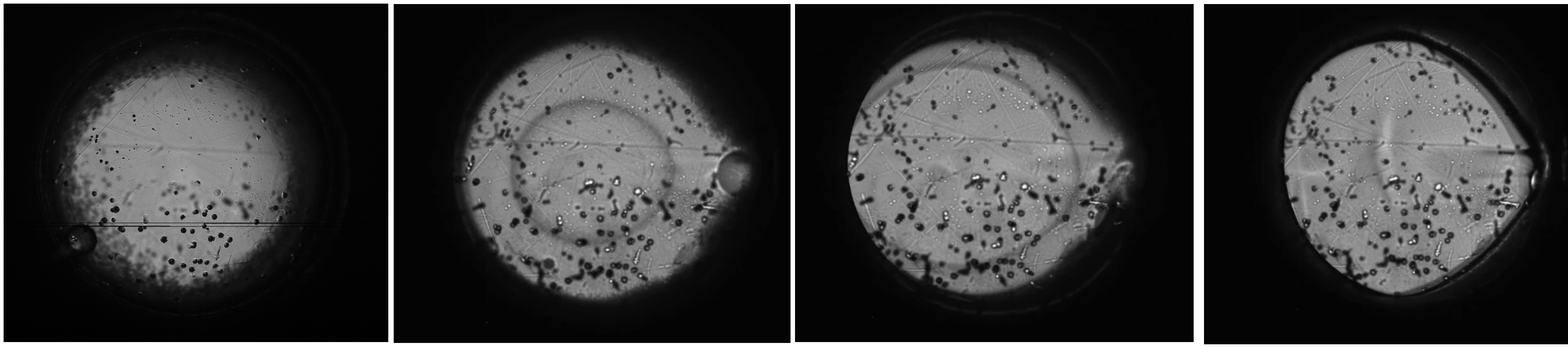
Partitioning Rates

- Partitioning calculations assume equilibrium… no information on effects of temperature ramp rates
- Approach to critical conditions was observed for different temperature ramp rates:

  0.5, 1.0, 2.0, 10, 15, 30, 50, 100 mK/min
- Different types of behavior were observed depending upon temperature ramp rate:

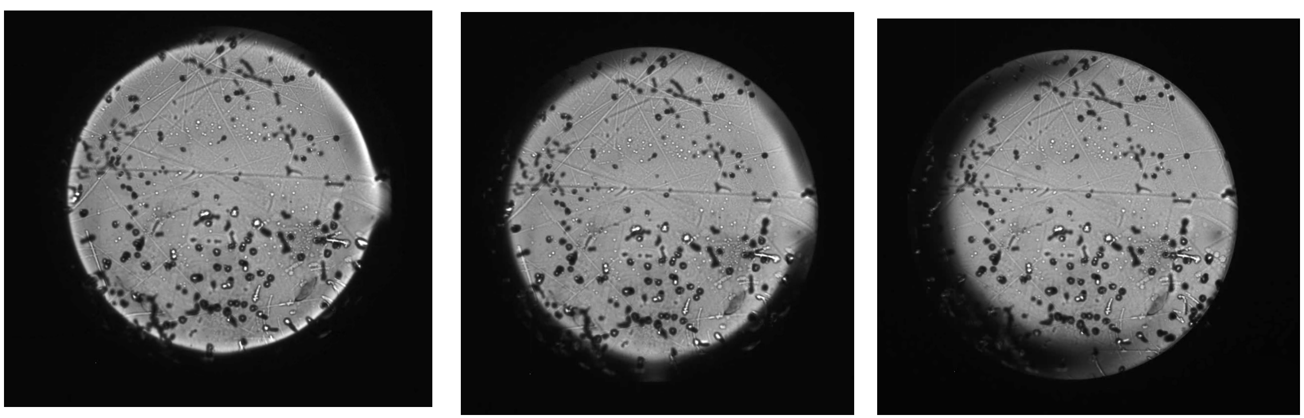
- fast rate , > 30 mK/min
- slow rate, < 10 mK/min
- intermediate rate ~ 10 -30 mK/min

Fast Ramp Rate > 10 mK/min



(a) (b) (c) (d)

(a) Vapor bubble expands (b), (c), (d) Liquid film on windows dries out with a denser phase around circumference

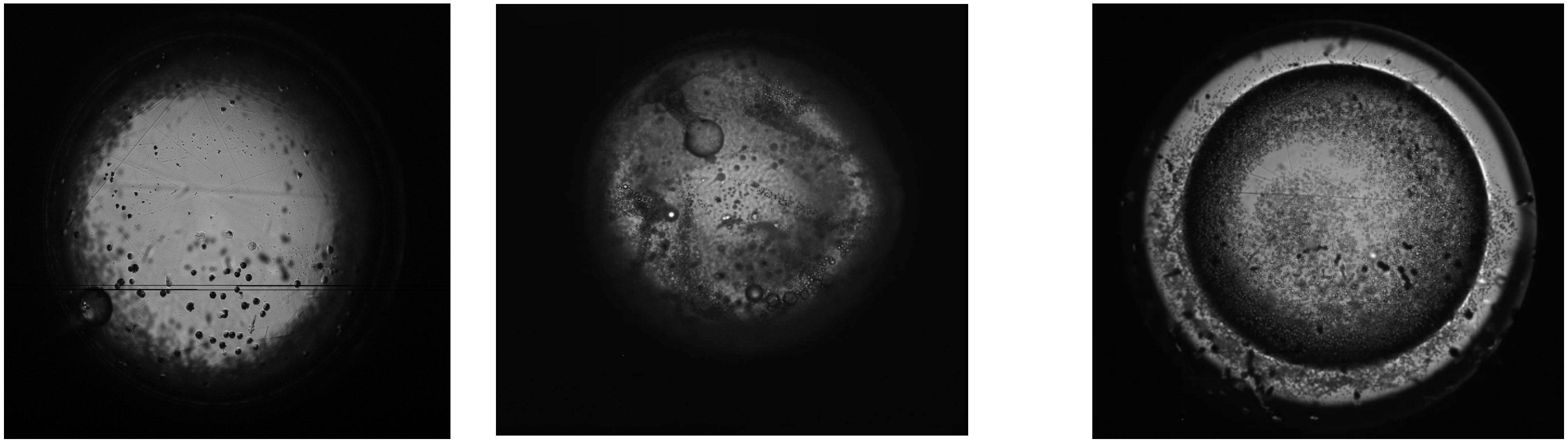


(e) (f) (g)

(e), (f), (g) Denser phase forms a crescent after equilibration

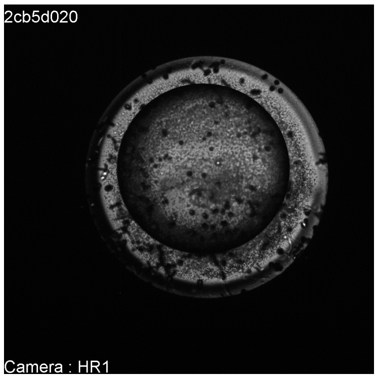
Temperature ranges from ~ Tc- 120 mK to Tc + 30 mK

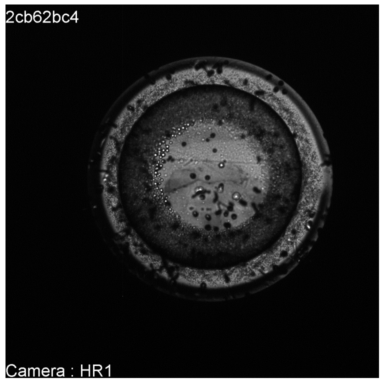
Slow Ramp Rate < 10 mK/min

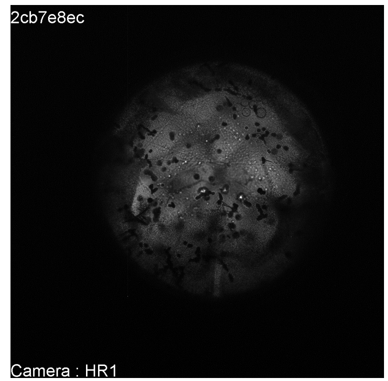


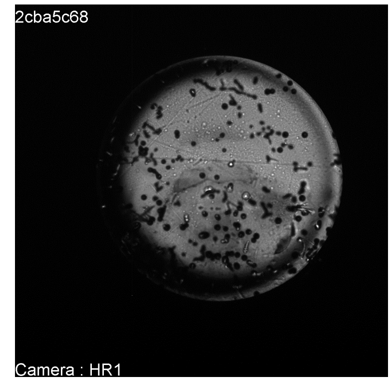
Expanding vapor bubble breaks with resulting motion with many small bubbles.
Over time a new vapor bubble is formed.

Slow Ramp Rate- Progression to Critical Transition (continued)





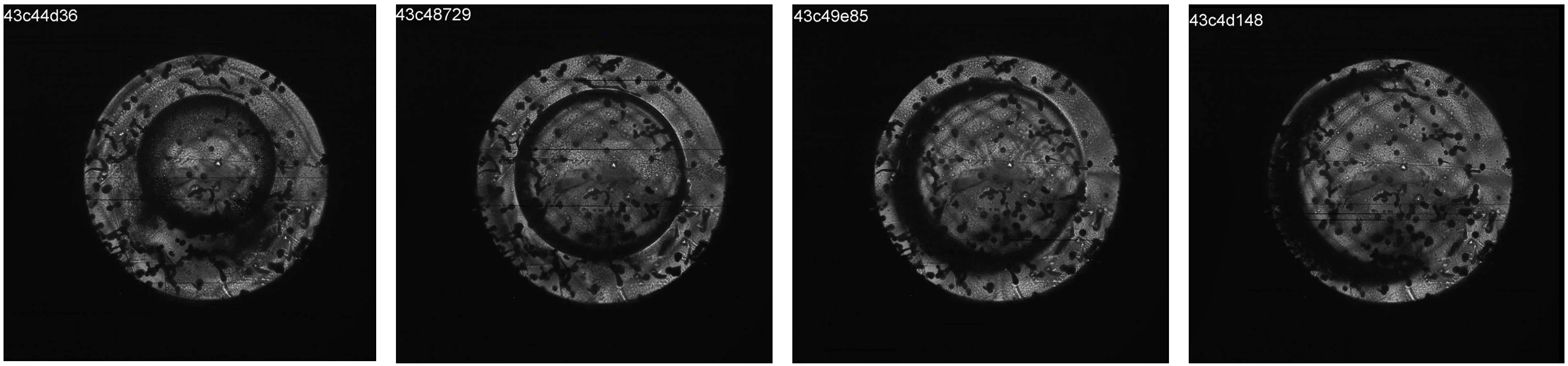




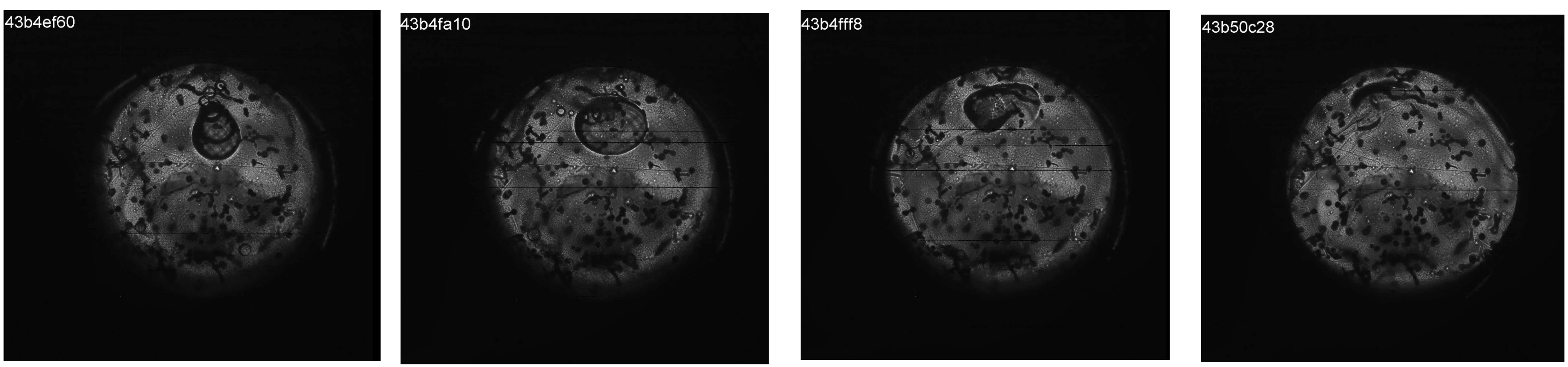
~ Tc -110 mK to Tc + 5 mK

Newly stabilized central vapor bubble collapses. After a period of unstable motion during temperature ramp up the fluid transitions through critical state.

Intermediate Ramp Rates



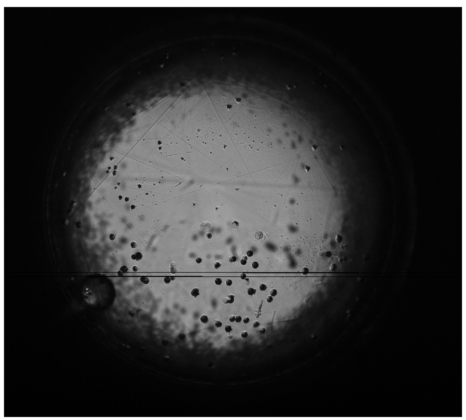
10 mK/min: Central bubble reforms and transitions to “single phase” with density gradient

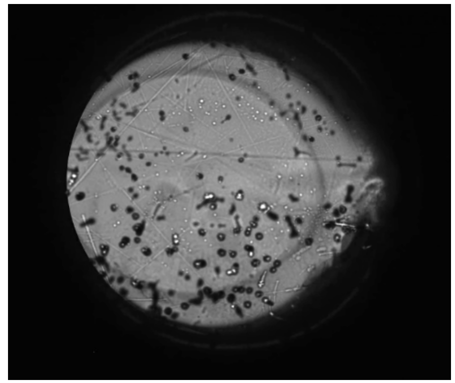


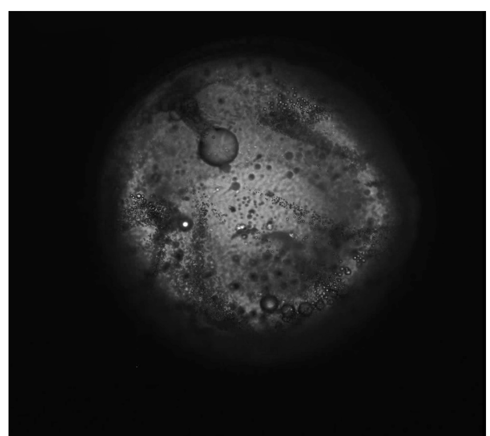
20 mK/min: Central bubble attempts to reform but fluid transitions without bubble reforming

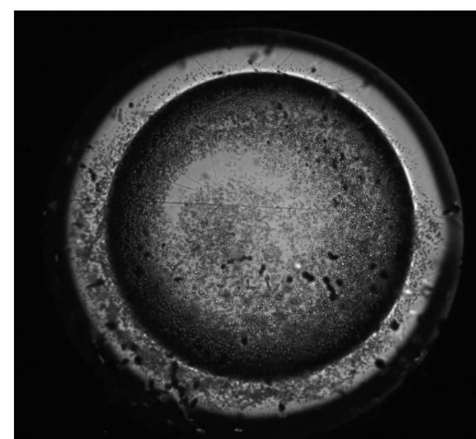
Fast vs Slow Ramp

Fast ramp



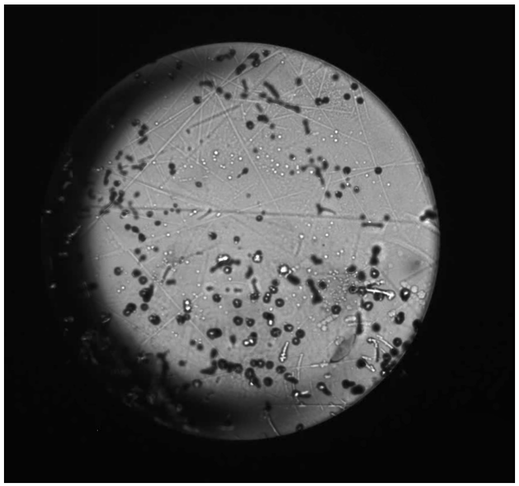






Slow ramp may enhance liquid-vapor partitioning

Appearance of Dense Phase



Possible reasons:

- Residual temperature gradient in cell
- Salt does not partition equally between liquid and vapor prior to critical transition
- Clustering of excess water molecules around unprecipitated salt ions
- Salt precipitate in fluid

Summary

- Experiments were conducted on the ISS under isochoric conditions for observing the phase behavior of a water- 0.5% w Na_2SO_4 solution in the near critical regime
- Incipient boiling starting at ~373 C is characterized by ~ 20 microns size bubbles travelling in channels toward the central vapor bubble
- Near critical phase behavior depends upon the heating rate:

  - For high heating rates (> 10 mK/min) the central vapor bubble expands with a denser phase around the boundary

  -For low heating rates (< 10 mK/min) the central bubble expands and breaks up with subsequent formation of a second stabilized vapor bubble. Transition to critical is characterized by the breaking of this central bubble

- Slower temperature ramp appears to improve the liquid –vapor partitioning
- Appearance of the denser phase near critical conditions may arise for a number of reasons

Acknowledgments

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