DESY

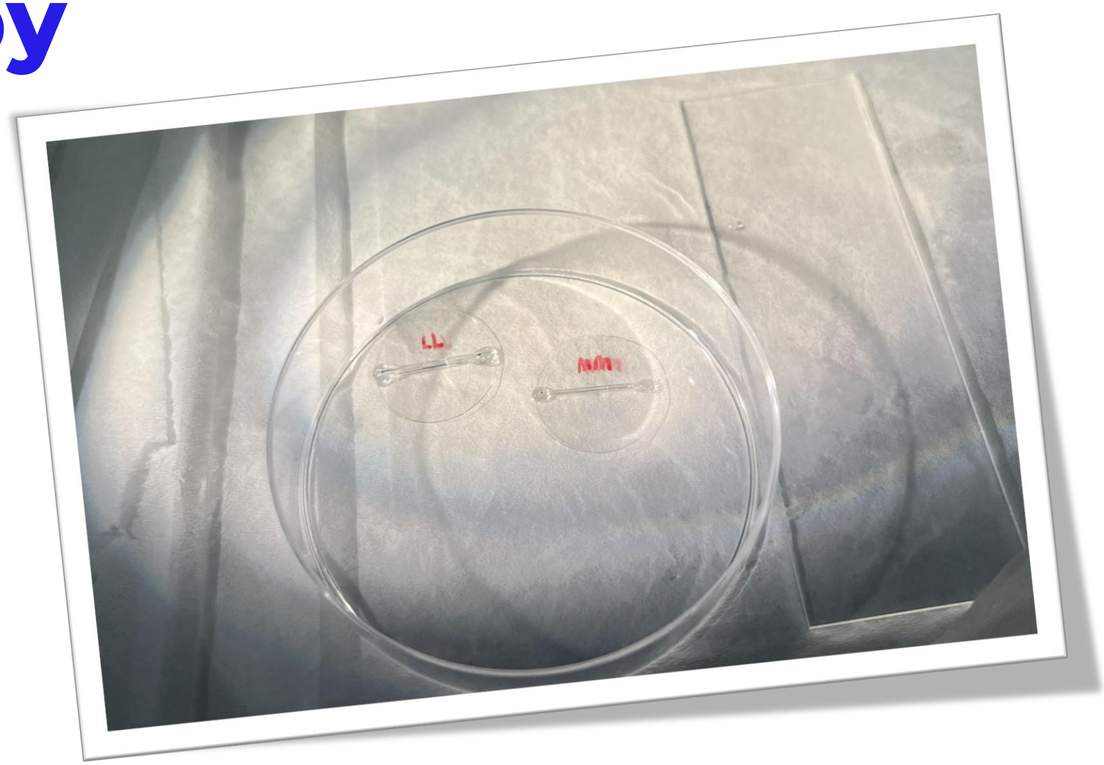
CMWS Centre for Molecular Water Science

Capillary Temperature Calibration for Raman Spectroscopy

Presented by: Kesini Chumphuthong

Supervised by: Dr. Claudia Goy

Group: Complex Liquids – FS-SMP

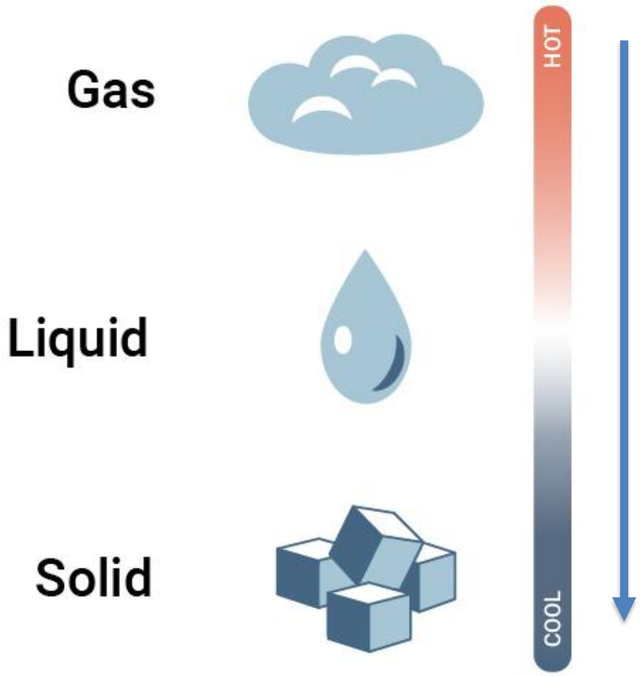


Overview

- Introduction
  - Phase transitions and anomalous behavior of H_2O
  - Raman Spectroscopy
- Experimental methods and setup
  - Raman microscope
  - Temperature cell
  - Sample preparation
- Results and challenges
- Outlook

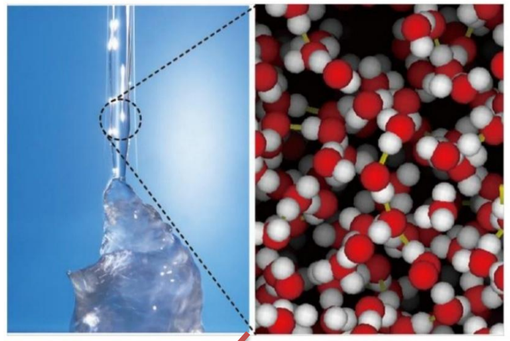
Phase transitions and anomalous behavior of water

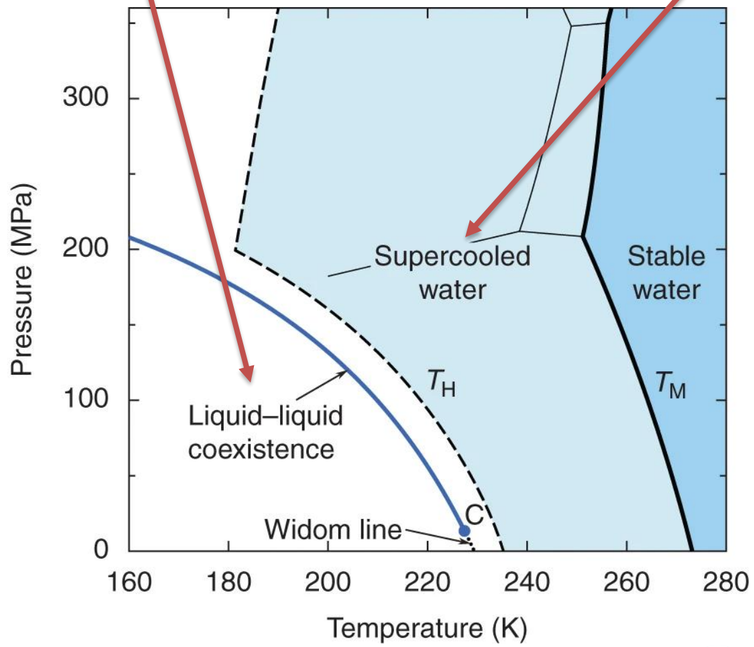
States of Matter



Liquid–liquid transition

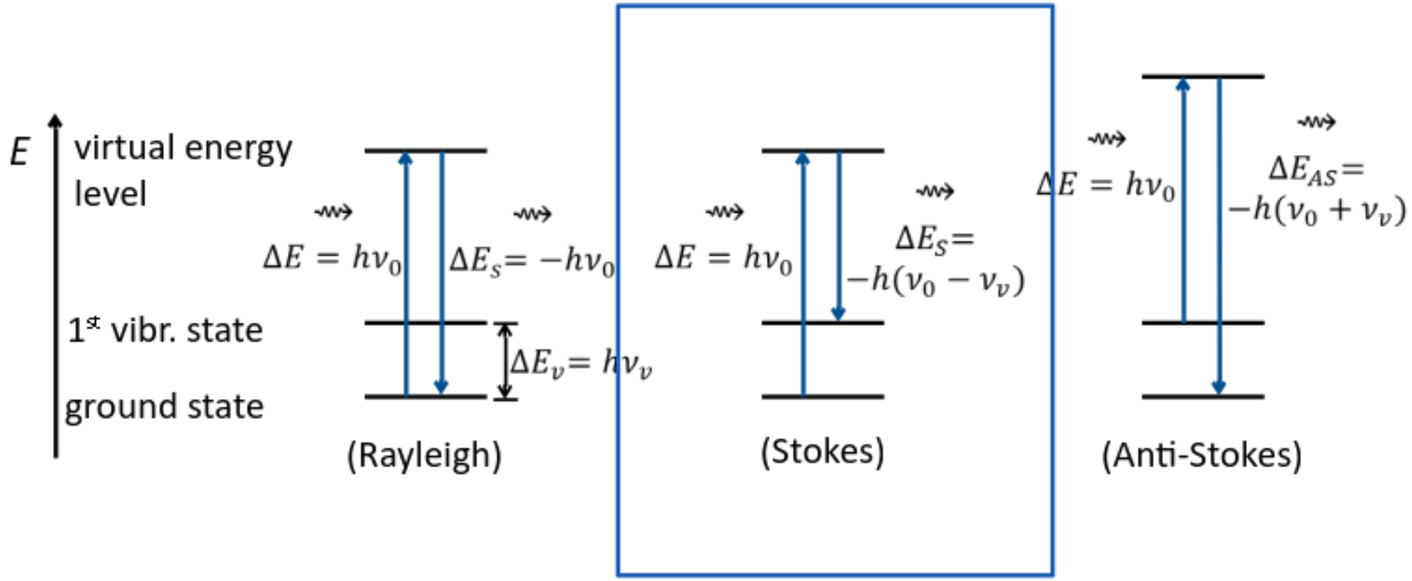
Supercooled liquid

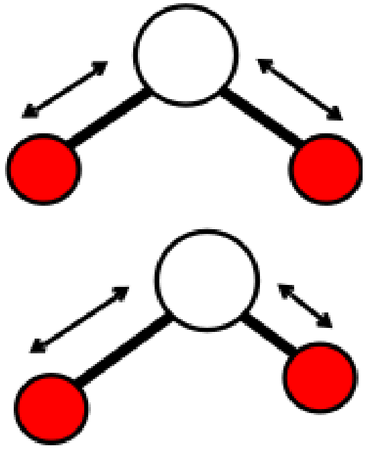




https://phys.org/news/2017-10-solution-mysterious-behavior-supercooled.html
https://www.sci.news/physics/phase-transition-supercooled-water-05801.html
https://www.breakingatom.com/learn-the-periodic-table/states-of-matter-solids-liquids-and-gases
Holten, V., Anisimov, M. Entropy-driven liquid–liquid separation in supercooled water. *Sci Rep* **2**, 713 (2012). https://doi.org/10.1038/srep00713

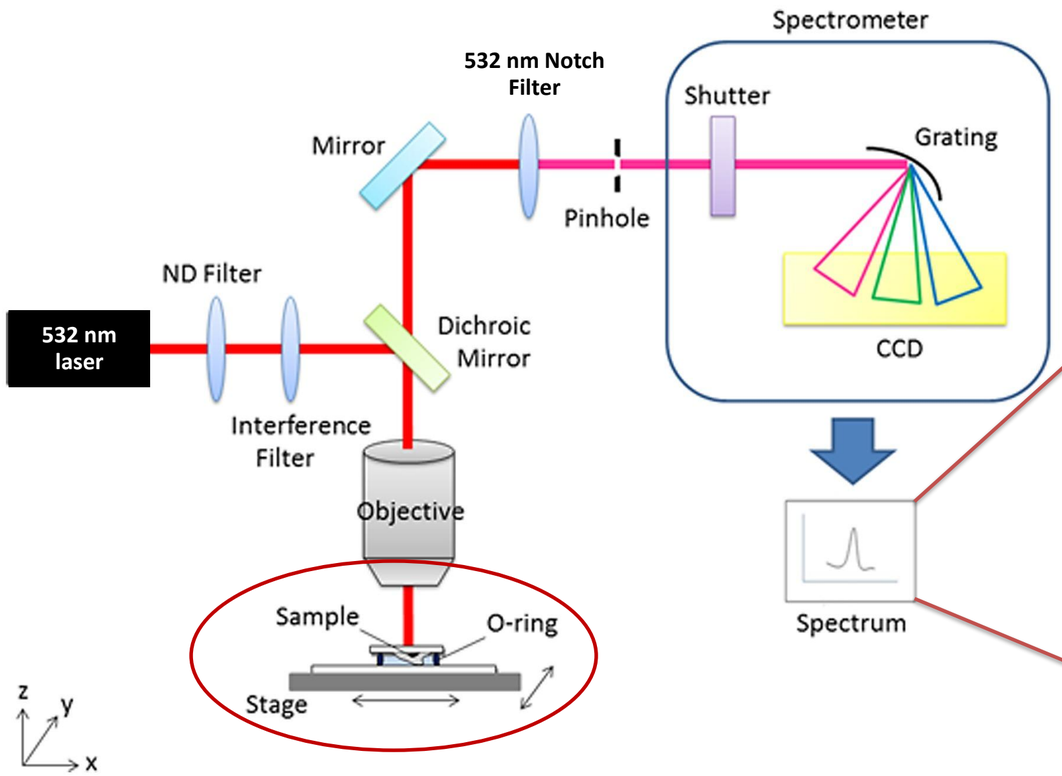
Raman spectroscopy

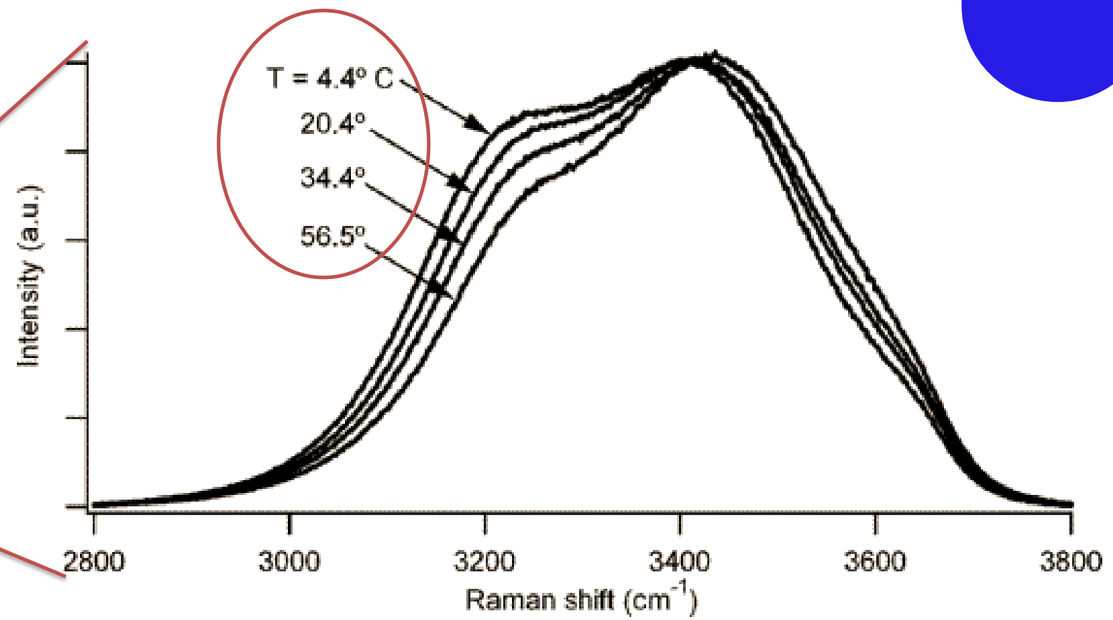




- probing vibrational and rotational modes
- molecular bond sensitive
- temperature, pressure and concentration dependent

Raman spectroscopy





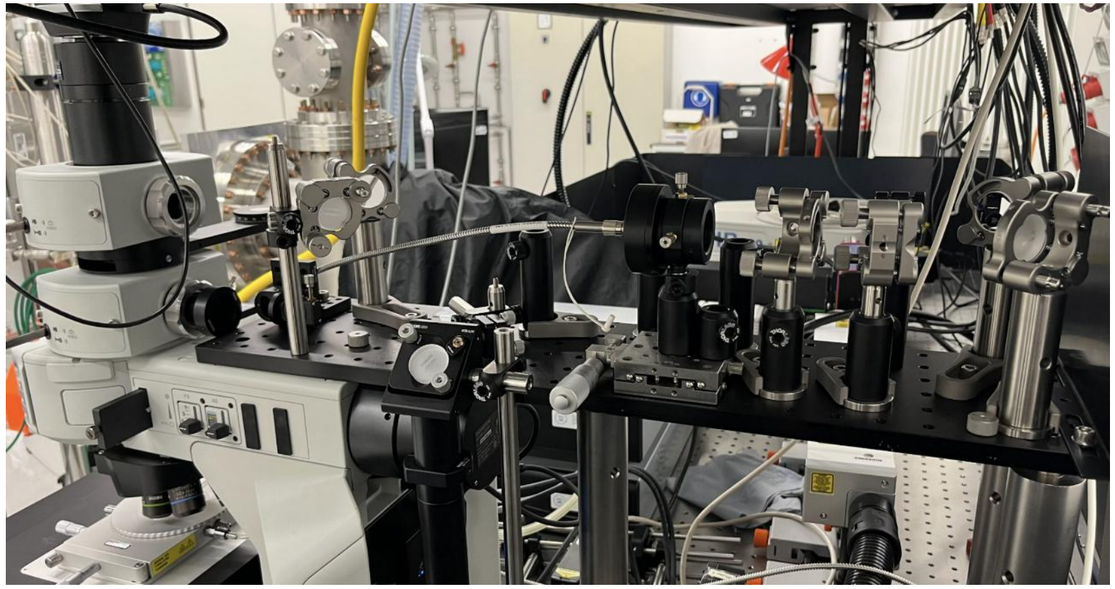
Schematic diagram of the Raman platform set-up

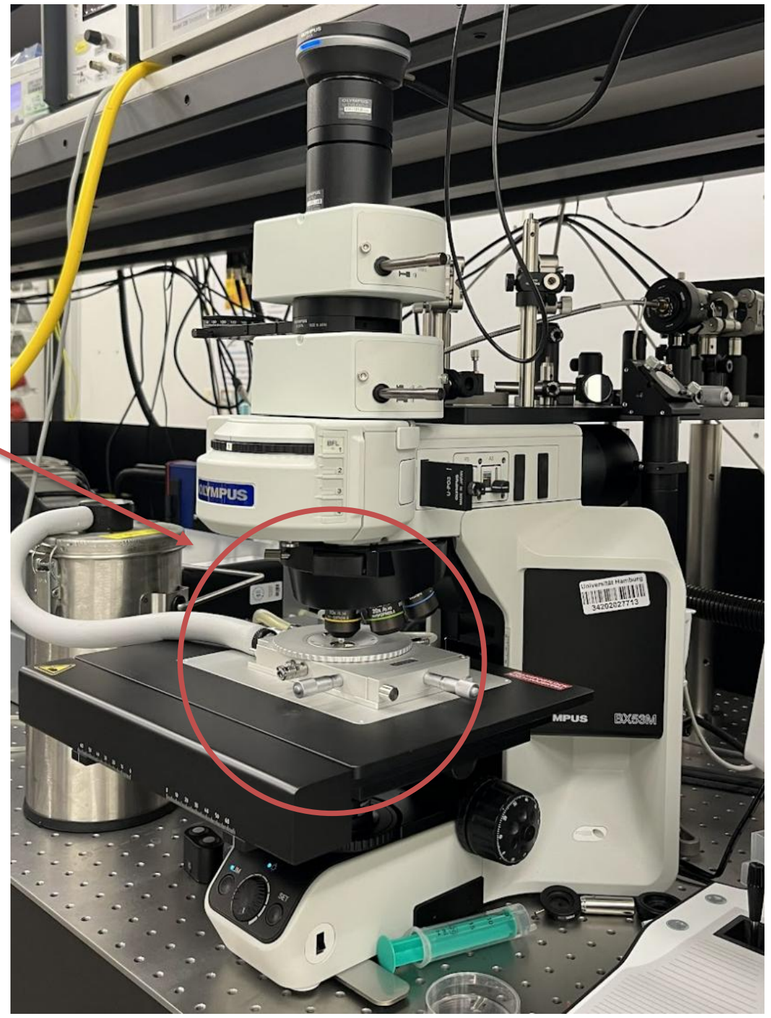
Hung, Pei-San; Kuo, Yi-Chun; Chen, He-Guei; Kenny Chiang, Hui-Hua; Kuang-Sheng Lee, Oscar (2015). Schematic diagram of the Raman platform set-up.. PLOS ONE. Figure.

Jared D. Smit et al./ Raman Thermometry Measurements of Free Evaporation from Liquid Water Droplets, J. Am. Chem. Soc, 2006, 128, 39, 12892–12898

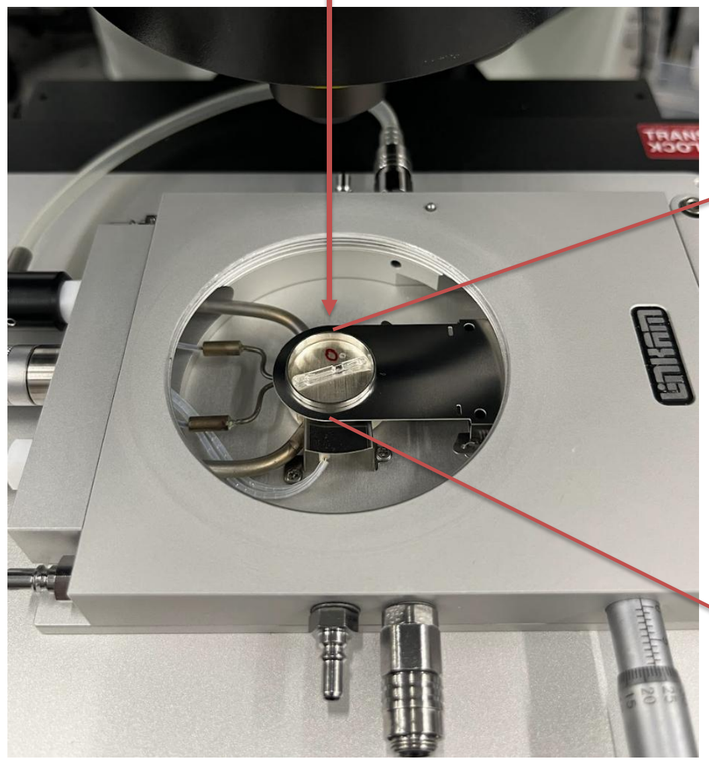
Raman microscope

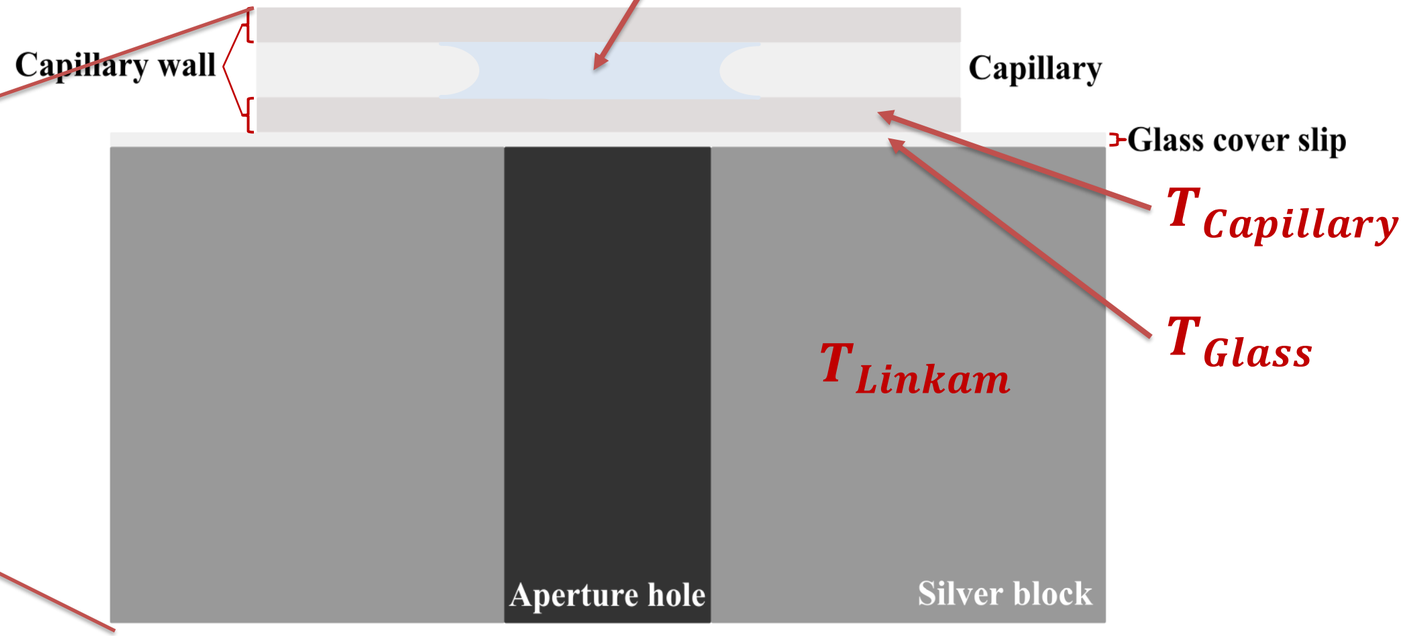
Linkam
Temperature cell





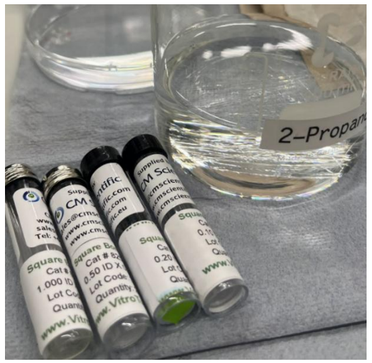
Temperature cell

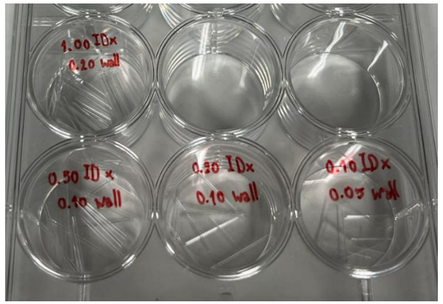


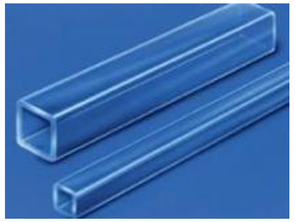


Capillary preparation

To clean and cut the capillaries



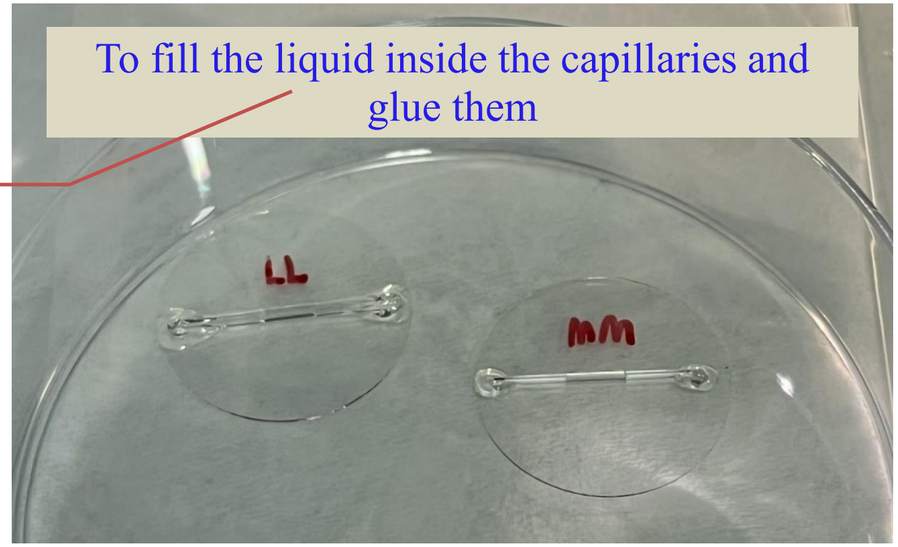




To place the capillary over the hole

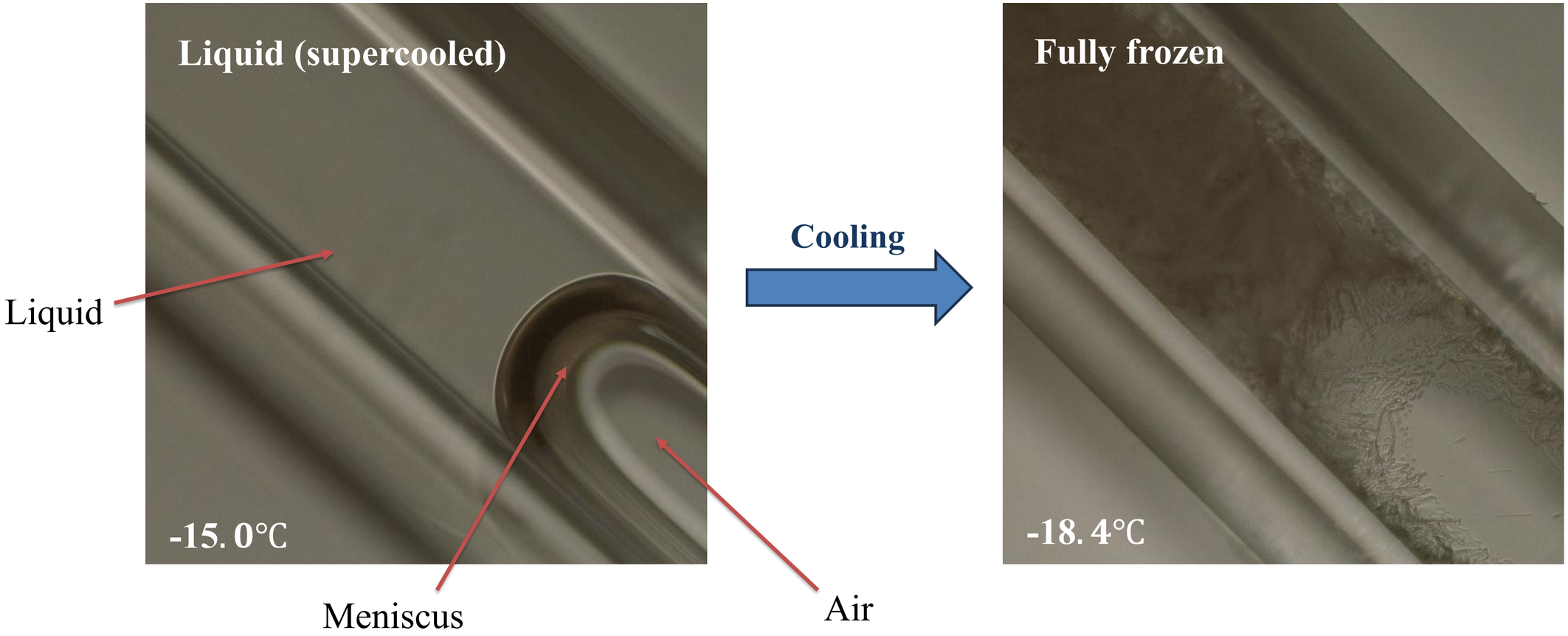
Substance	NIST Melting Point (°C) (Reference)	Sharpness of Melting Point
Pure water	0.0	Very Sharp
1-Undecene	−49.4	Moderate
n-Decane	−29.7	Sharp
n-Dodecane	−9.6	Very Sharp

To fill the liquid inside the capillaries and glue them



Melting point study

Preparation: Phase transition of n-Dodecane at the literature melting point: -9.6°C (NIST)



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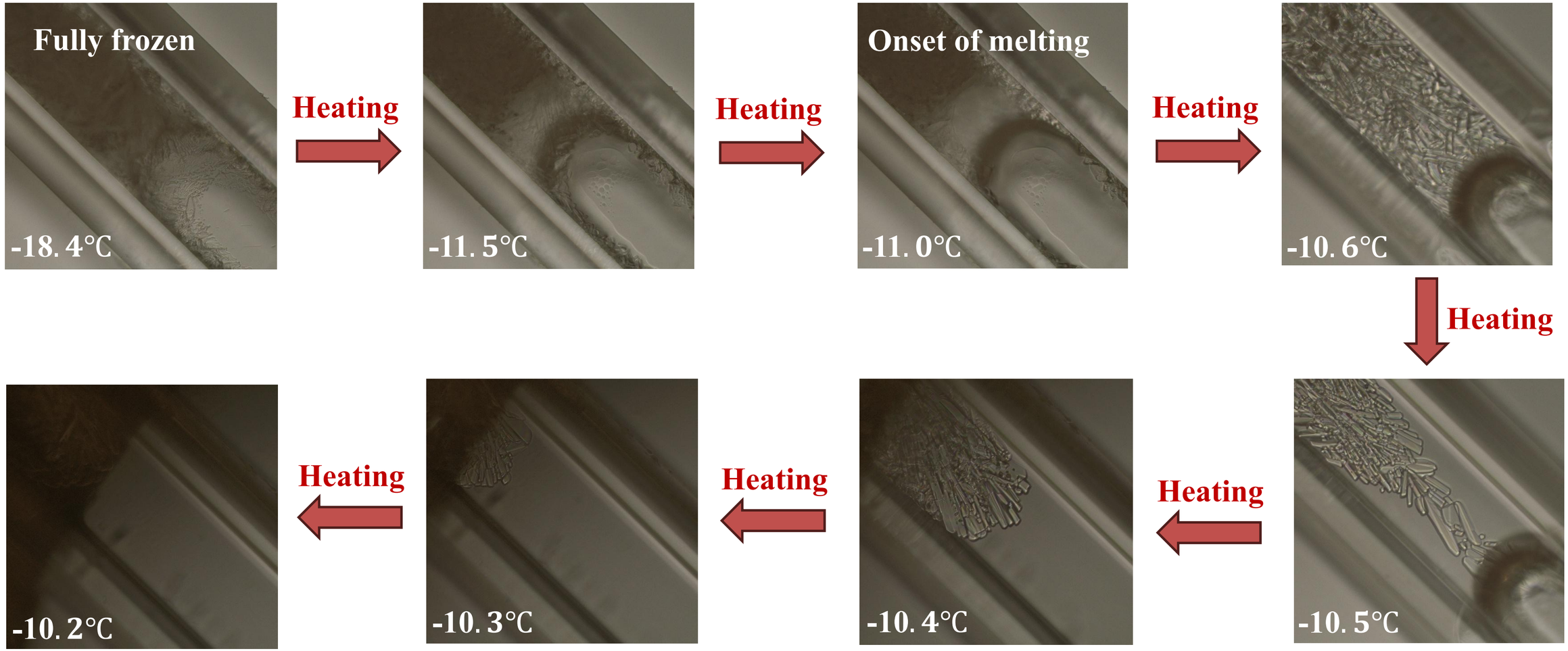
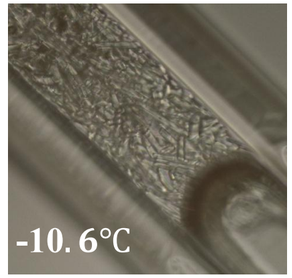
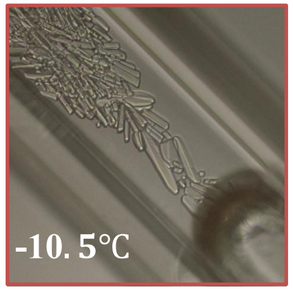
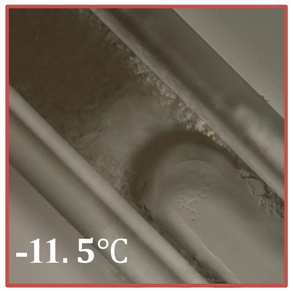
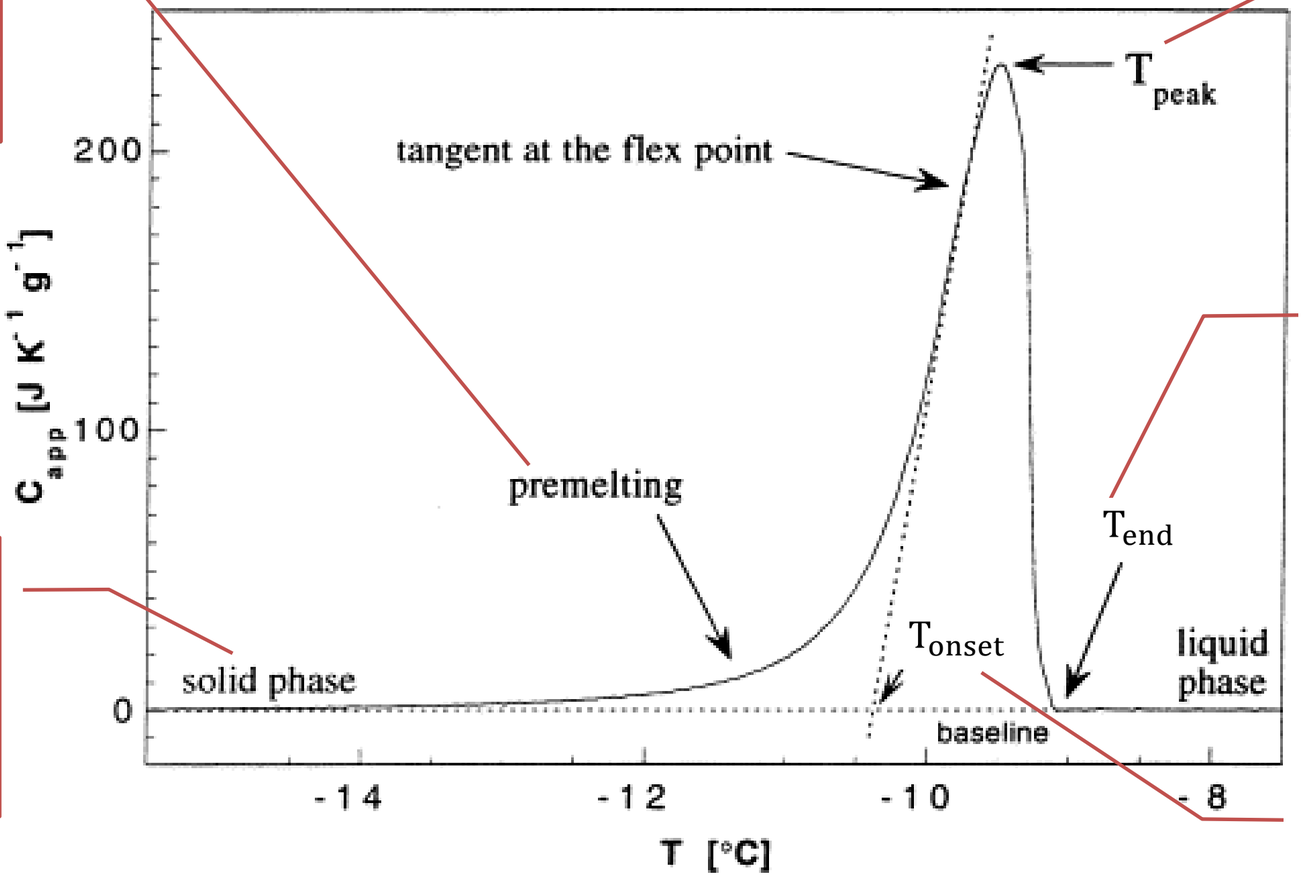


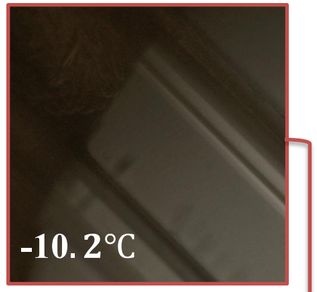
Melting point analysis

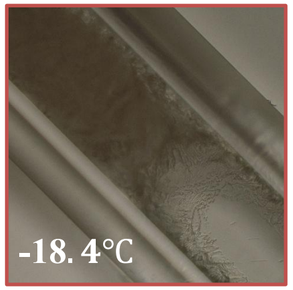


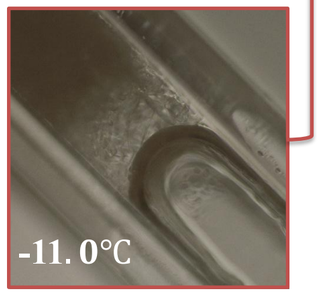








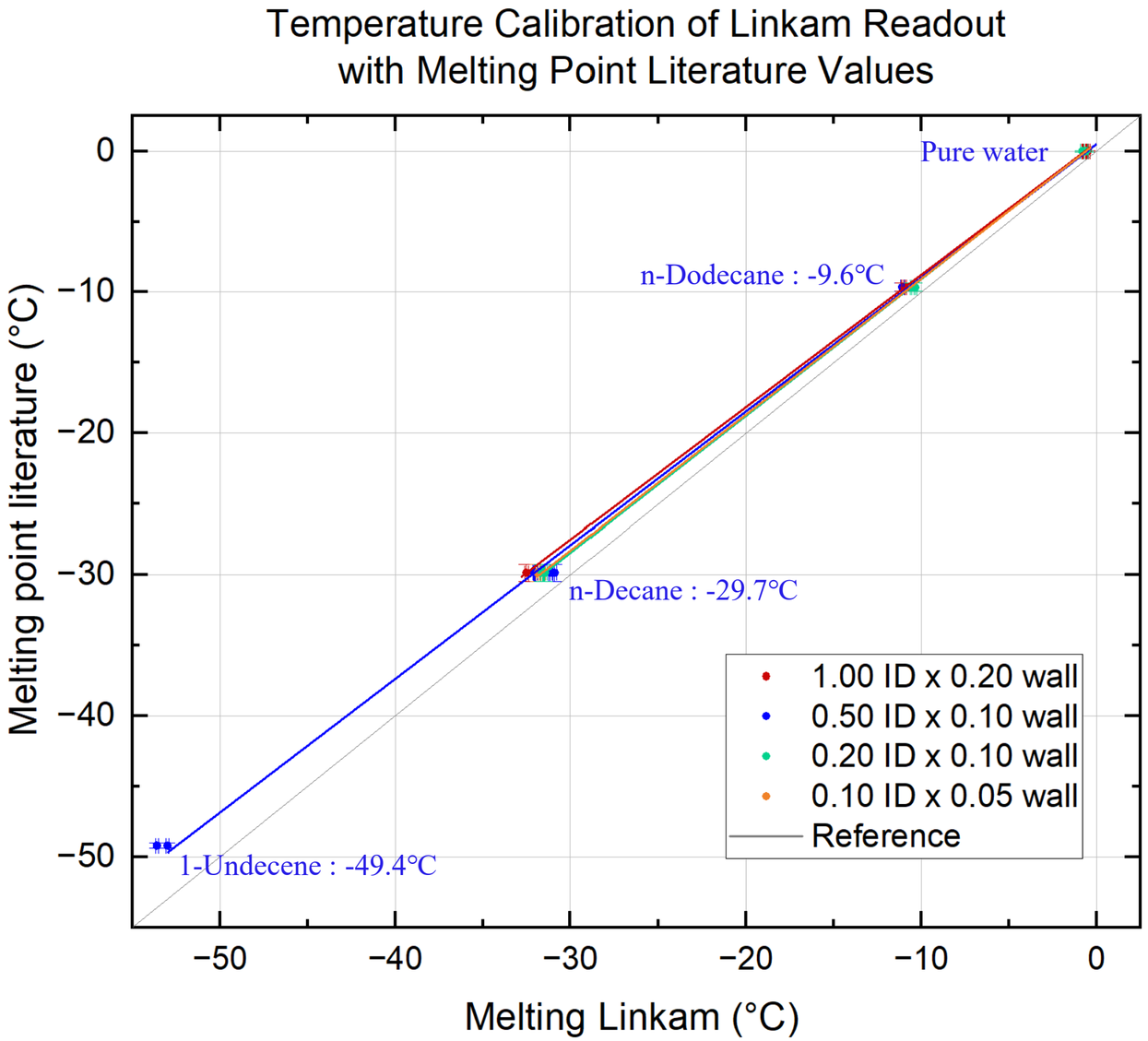


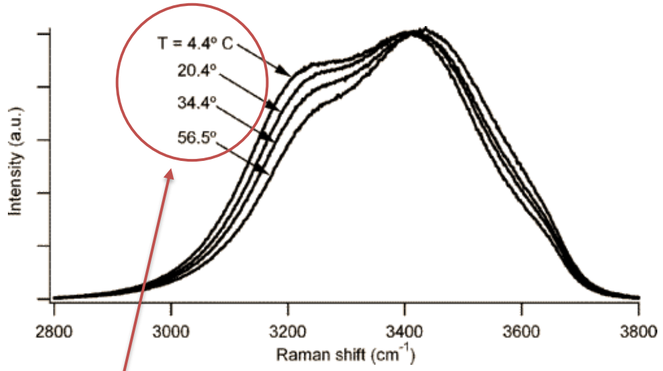


$$T_{Linkam} = \frac{T_{onset} + T_{end}}{2}$$

C Cardelli et al./ n-Dodecane melting studied by the combined use of different calorimetric modes, Thermochimica Acta, 2000, Volume 364, Issues 1–2, Pages 1-10

Results





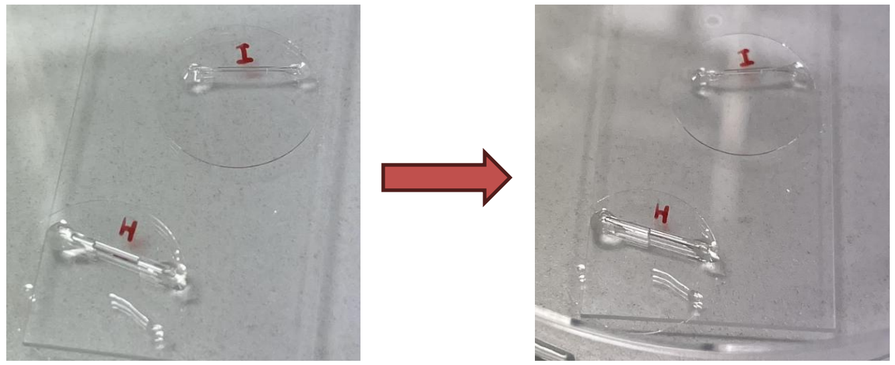
- ✓ Set up procedure for calibration
- ✓ Linear progression for 4 sizes of capillaries:

$$T_{real} = a + bT_{Linkam}$$

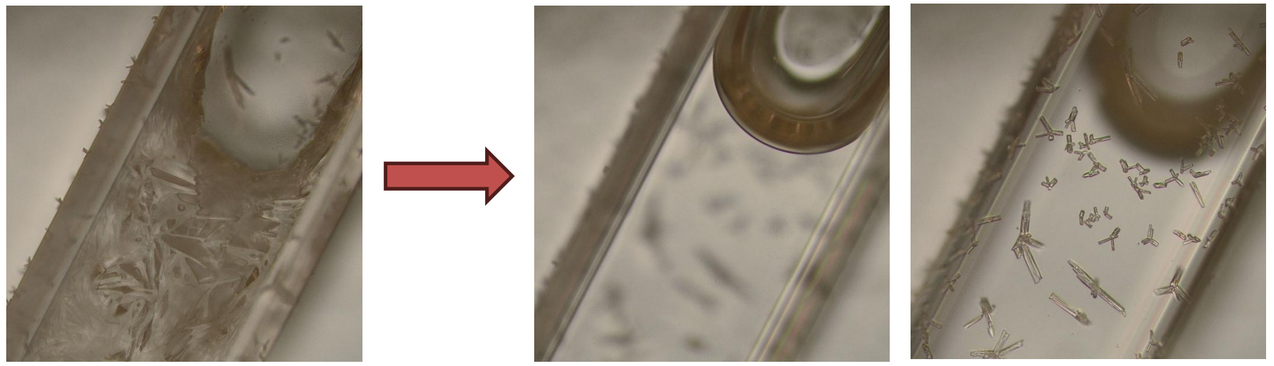
Capillary	a	b
1.00 ID x 0.20 wall	-0.64485	1.0668
0.50 ID x 0.10 wall	-0.53506	1.05586
0.20 ID x 0.10 wall	-0.63386	1.03245
0.10 ID x 0.05 wall	-0.61329	1.03913

Experimental challenges

- Challenge of liquid insertion into capillaries



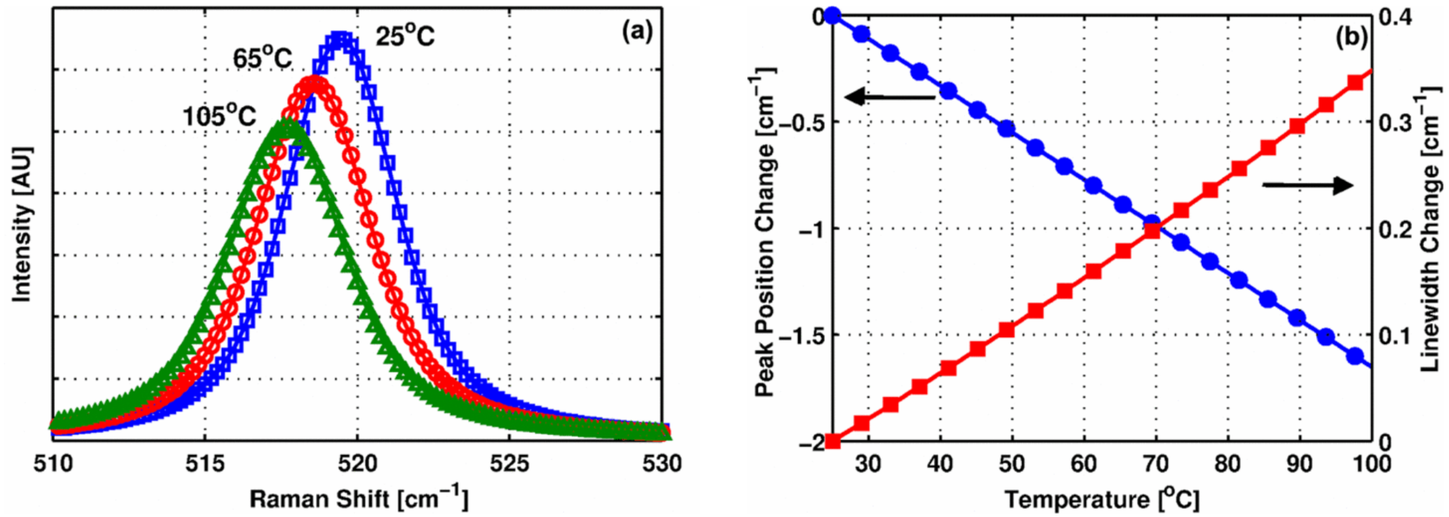
- Leakage of liquid from the capillary



- Anomalous behavior of liquids

Outlook

- Extend the temperature range using substances with different melting points: Dimethyl sulfoxide (DMSO): 18.5°C, n-Undecane: -26.0 °C, Isopropanol: - 89.5 °C
- Increase statistics
- Other capillary shapes and materials (rectangular, fused silica)
- Temperature measurement based on sharp Raman lines



Saltonstall, Christopher & Serrano, Justin & Norris, Pamela & Hopkins, Patrick & Beechem, Thomas. (2013). Single element Raman thermometry. The Review of scientific instruments. 84. 064903. 10.1063/1.4810850.

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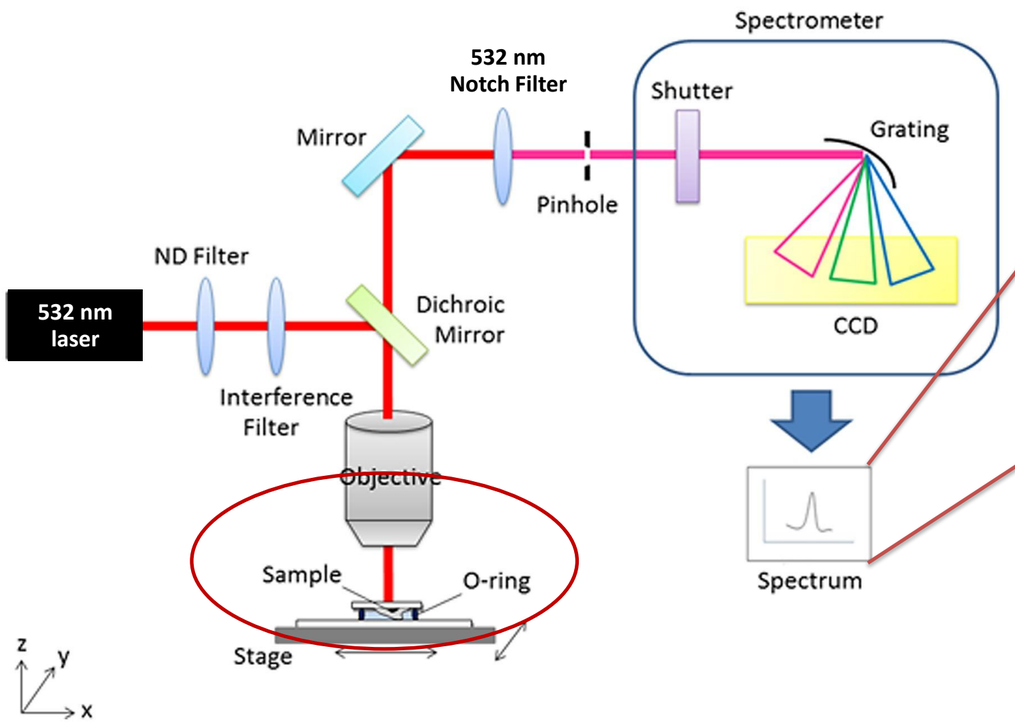
Questions?

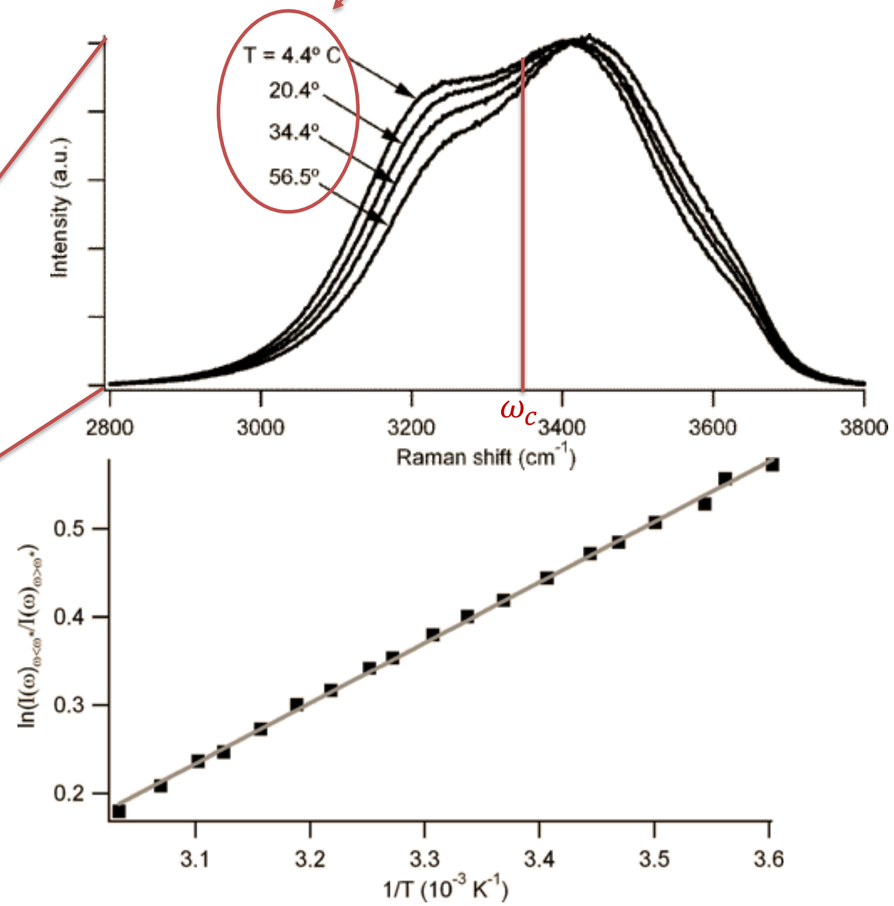
Raman microscope



Schematic diagram of the Raman platform set-up

Hung, Pei-San; Kuo, Yi-Chun; Chen, He-Guei; Kenny Chiang, Hui-Hua; Kuang-Sheng Lee, Oscar (2015). Schematic diagram of the Raman platform set-up.. PLOS ONE. Figure.

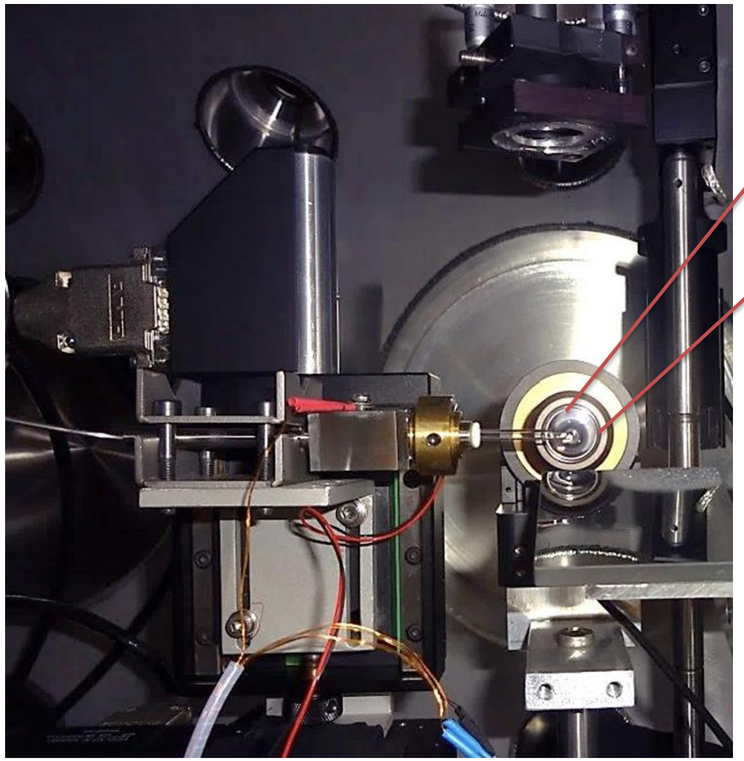
The linear progression for temperature calibration: $T_{real} = a + bT_{Linkam}$

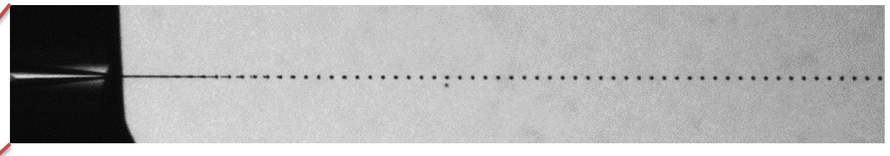


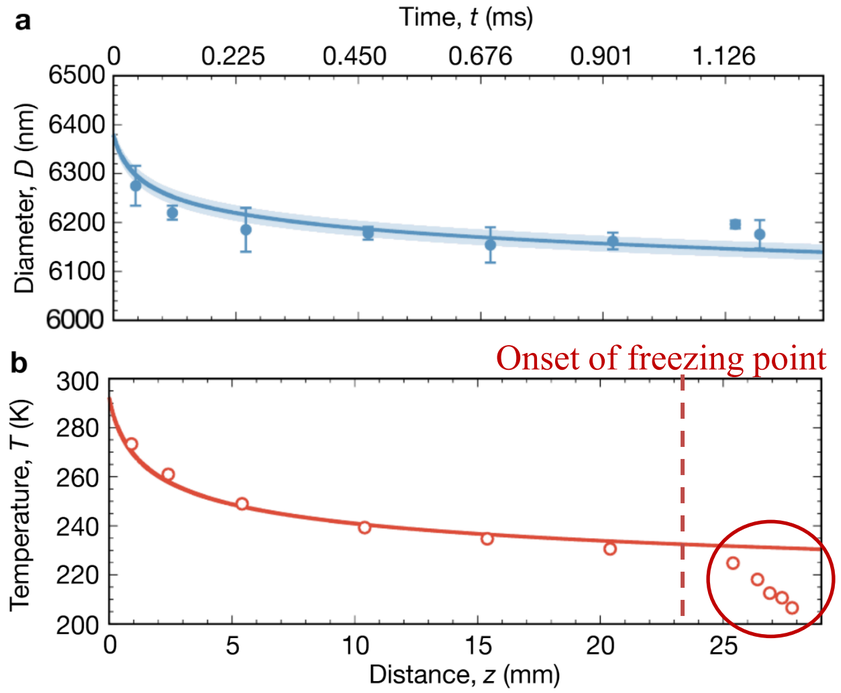
The empirical relation between band intensity: $\frac{1}{T} = \ln\left(\frac{I_{\omega<\omega_c}}{I_{\omega>\omega_c}}\right)$

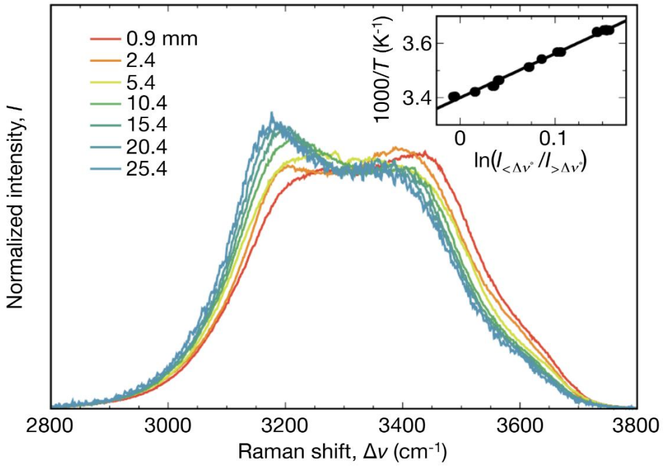
Jared D. Smit et al./ Raman Thermometry Measurements of Free Evaporation from Liquid Water Droplets, J. Am. Chem. Soc, 2006, 128, 39, 12892–12898

Liquid jet system in vacuum









$$\frac{1}{T} = \ln\left(\frac{I_{\omega<\omega_C}}{I_{\omega>\omega_C}}\right)$$

Claudia Goy et al./ Shrinking of Rapidly Evaporating Water Microdroplets Reveals their Extreme Supercooling, Physical Review Letters, 2018 120. 015501. 10.1103/PhysRevLett.120.015501.

Literature Review

- Substances for temperature calibration

Substance	NIST Melting Point (°C) (Reference)	Sharpness of Melting Point
Pire water	**0.0**	Very Sharp
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n-Decane	−29.7	Sharp
n-Dodecane	−9.6	Very Sharp
n-Undecane	-26.0	Sharp
Isopropanol	-89.5	Sharp
Dimethyl sulfoxide	18.5	Sharp