Pacific Northwest
NATIONAL LABORATORY

Exploring “No-Man’s Land”

An Examination of Water Between -44°F and -190°F

August 18, 2020

Loni Kringle

Post-Doctoral Research Associate

Pronouns: she/her

U.S. DEPARTMENT OF ENERGY BATTELLE

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https://www.surveymonkey.com/r/PNNL081820

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1 of 17

U.S. DOE Labs

Pacific Northwest
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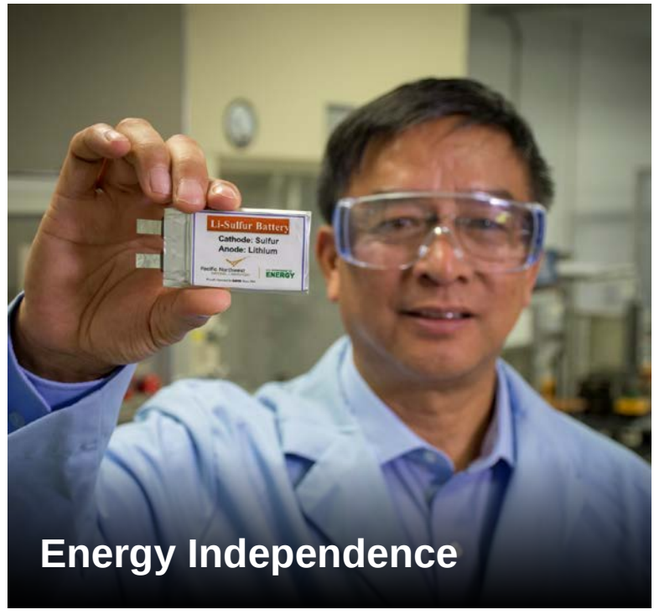
PNNL is Focused on **DOE's MISSIONS** and Addressing Critical **NATIONAL NEEDS**

Scientific Discovery



Energy Independence


National Security

Environmental Management

Pacific Northwest
NATIONAL LABORATORY

PNNL is an ECONOMIC ENGINE

4,722
Employees

265
Inventions

$1.46B
Total Economic Output

$1.01B
Annual Spending

88
Patents

7,180
Jobs Generated
in Washington

$465M
Total Payroll

34
Licenses

193
Companies
with PNNL Roots

Pacific Northwest
NATIONAL LABORATORY

50+ Years

Developing Goodwill

Decades	**$28.5M**	**347,000**	**>120**
FY19	**$0.52M**	**30,000**	**56**
	Philanthropic Investments	**Team Battelle Volunteer Hours**	**Community Organizations**

My Path to Pacific Northwest National Lab

Rice Lake, WI

Photo Credit: Dale Kringle

My Path to Pacific Northwest National Lab

Rice Lake, WI

Waverly, IA

- Wartburg College
- B.A. Chemistry and Physics

Photo Credit: www.wartburg.edu

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Eugene, OR

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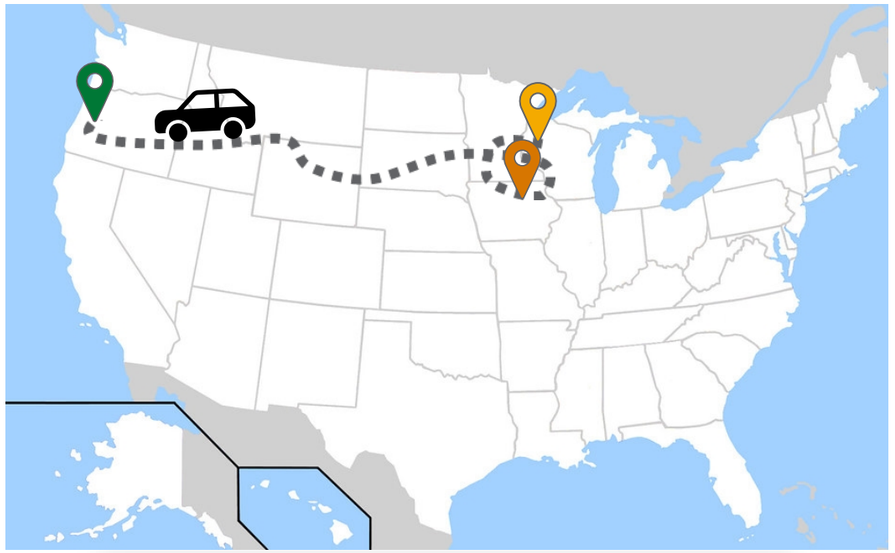

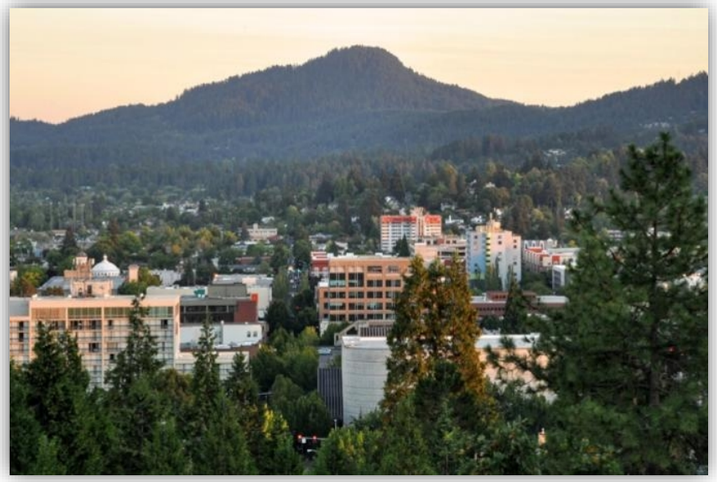

Photo Credit: www.eugenecascadescoast.org

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- Wartburg College
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Eugene, OR

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Richland, WA

- Pacific Northwest National Lab
- Post. Doc. Chemical Physics
- Started January 2019
- STEM Ambassador

Photo Credit: Pacific Northwest National Lab

Water is very important, and it is everywhere

At PNNL we study the fundamental properties of water under extreme conditions

- Supercooled
- Low pressure
- At interfaces

The quest to understand water

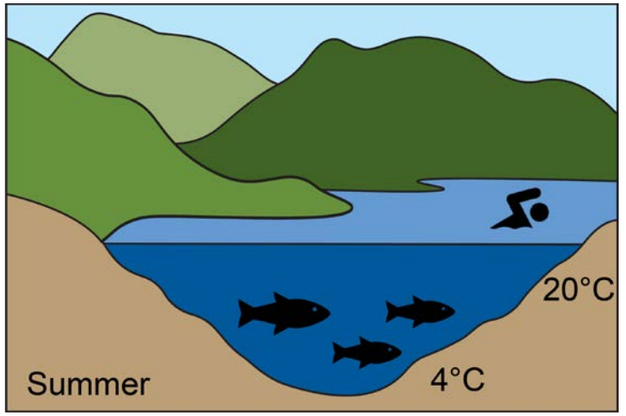
"Enormous effort has been invested in experimental determinations of the properties of water… Despite the effort, our factual knowledge is meager and our understanding rudimentary."

Narten, Venkatesh, and Rice, *J. Chem. Phys.* **64**, 1106 (1976).

We are familiar with water's anomalies, but we don't always recognize them as strange

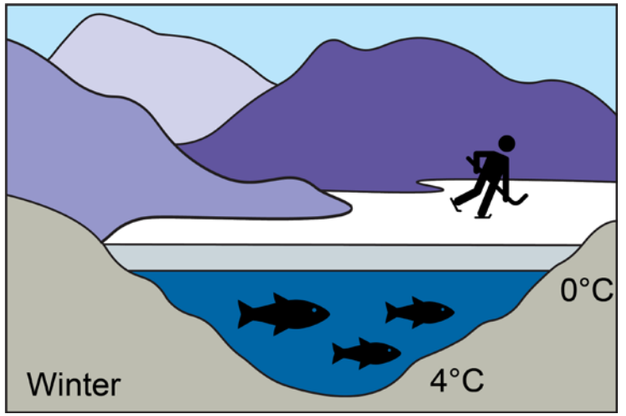
Solid ice floats in liquid water

- Density maximum at 4°C (39.2°F)



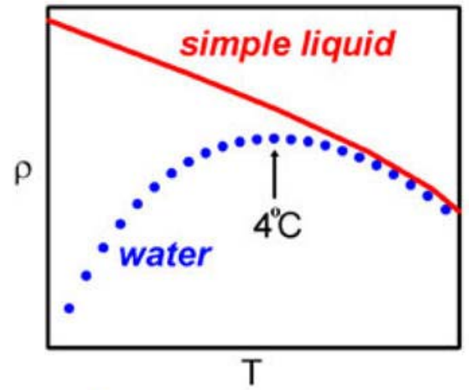
Water expands when freezing to ice

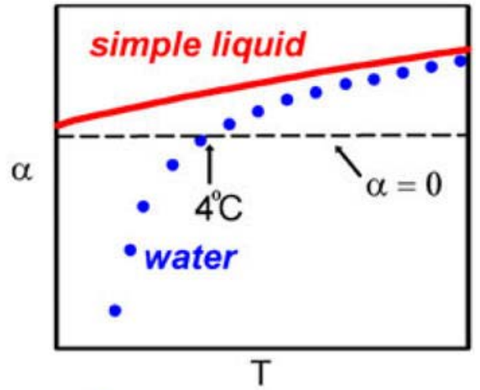
- Increase in volume with decrease in entropy



Water's anomalies become more pronounced at low temperatures

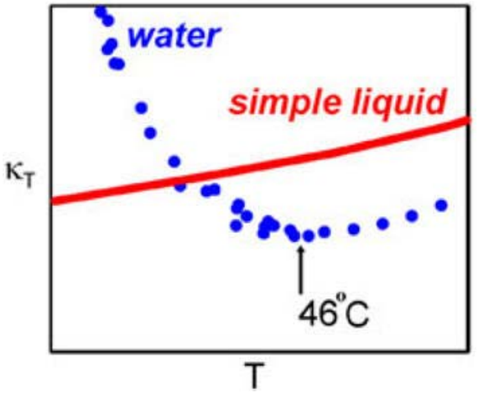
Density

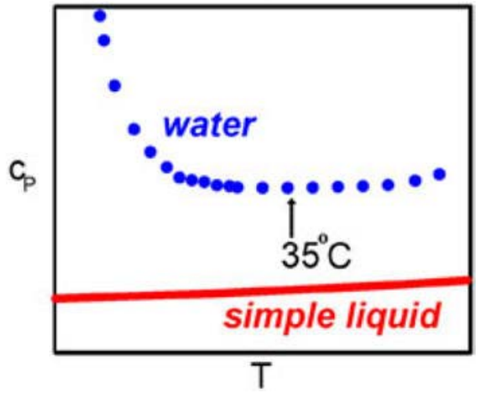




Thermal Expansion

Isothermal Compressibility





Isobaric Heat Capacity

Gallo et al. *Chem. Rev.* **116**:7463 (2016).

Why should we care about water in extreme environments?

Materials Science

- Catalysis
- Energy capture and storage

Biology and Biophysics

- Pharmaceuticals
- Protein folding and DNA replication

Meteorology

- Cloud formation

Astrochemistry

- Interstellar dust and comet composition

The states of matter

Gas

Conforms to the shape of its container

Expands to fill container

Liquid

Conforms to the shape of its container

Constant volume

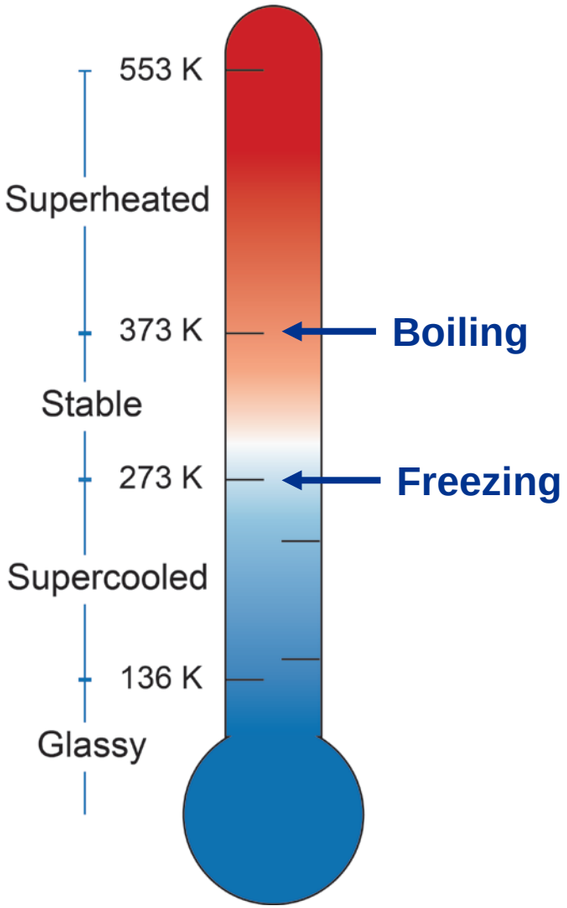
Solid

Definite Shape

Definite Volume

Crystalline Solids

Temperature regimes for liquid water



°C = K - 273.15

°F = (K - 273.15) × 9/5 + 32

Stable

- Liquid water between the boiling and freezing points

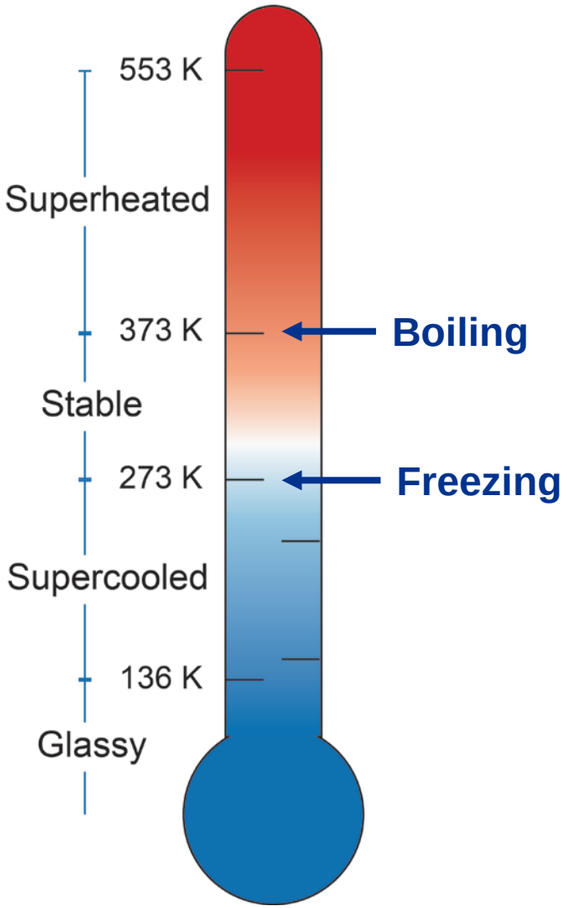
Supercooled

- Liquid water cooled below the freezing point, without it becoming solid

Glassy

- Mechanical properties of a solid but the molecular structure of a liquid – no long-range order

Temperature regimes for liquid water



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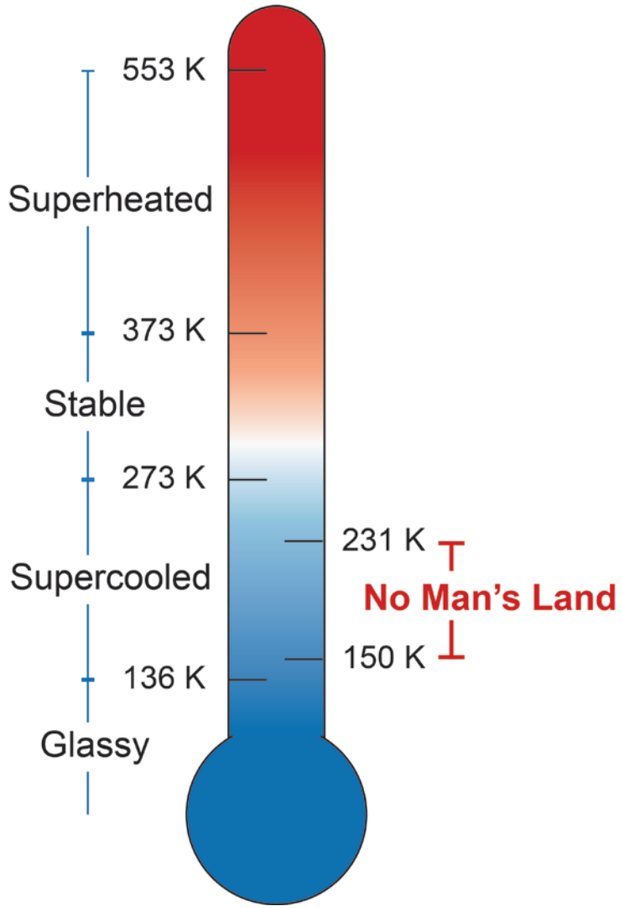
Glass Like

Crystalline Like

Water’s “No Man’s Land”



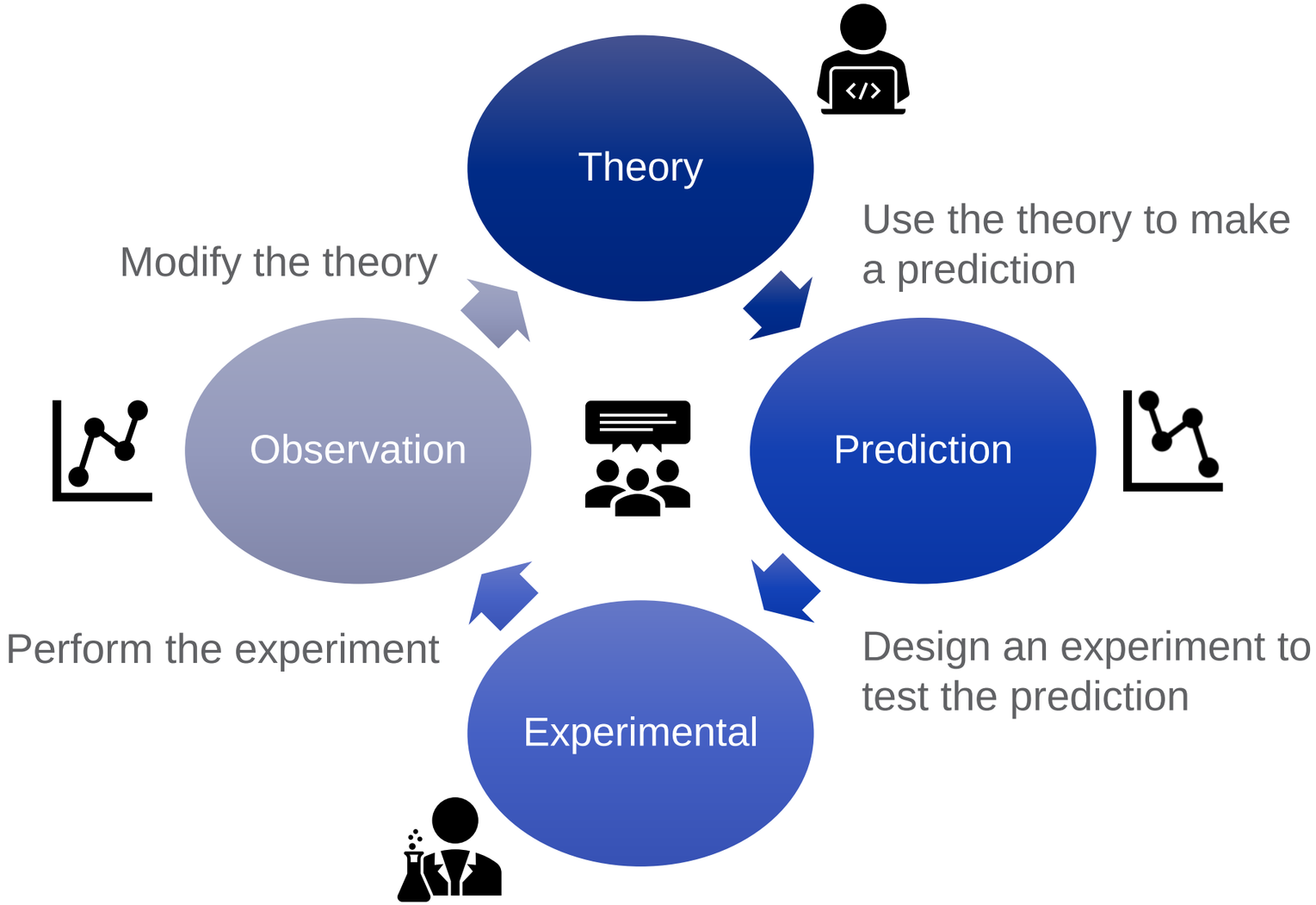
°C = K - 273.15

°F = (K - 273.15) × 9/5 + 32

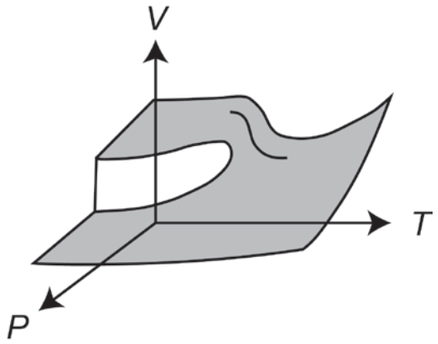
Rapid crystallization limits experimental investigation

- Not an absolute limit but a technological one
- Experimental observation time needs to be faster than the crystallization time
  - Very fast steps
  - Delay crystallization

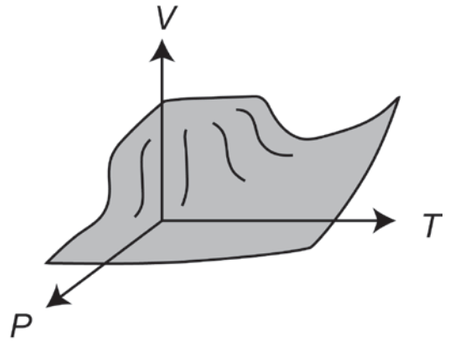
Theories explain and predict experimental observations



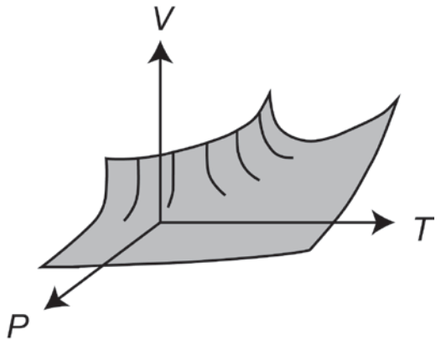
Different theories of water in “No Man’s Land”



Liquid-Liquid Phase-Transition Hypothesis

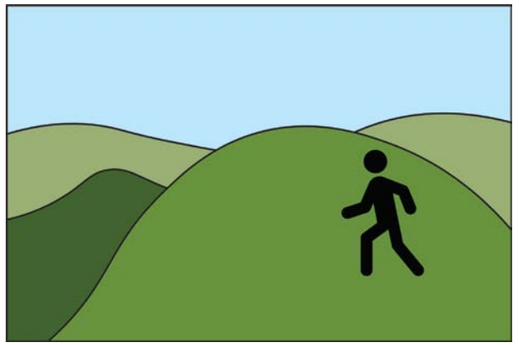


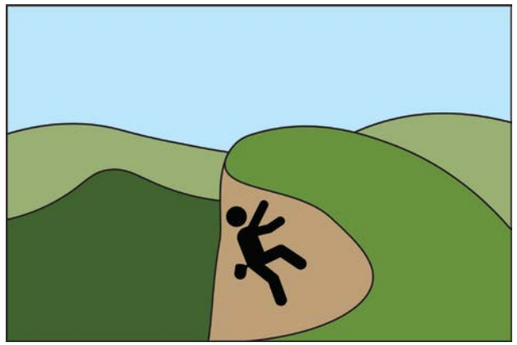
Singularity-Free Hypothesis



Stability Limit Hypothesis

Is there a hill or is there a cliff?





Mishima and Stanley, *Nature* **396**:329 (1998).

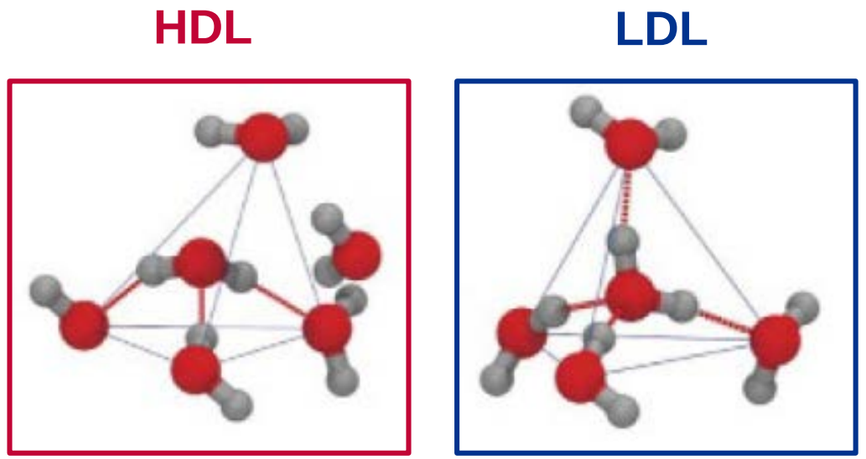
Two “Species” of Water; High-Density Liquid and Low-Density Liquid

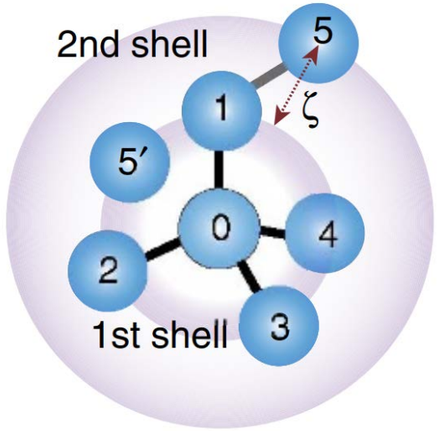
Low-Density Liquid Water (LDL)

- Tetrahedral arrangement
- 4 nearest neighbors in the 1st shell

High-Density Liquid Water (HDL)

- Closely packed non-nearest neighbor
- “Collapsed” second shell



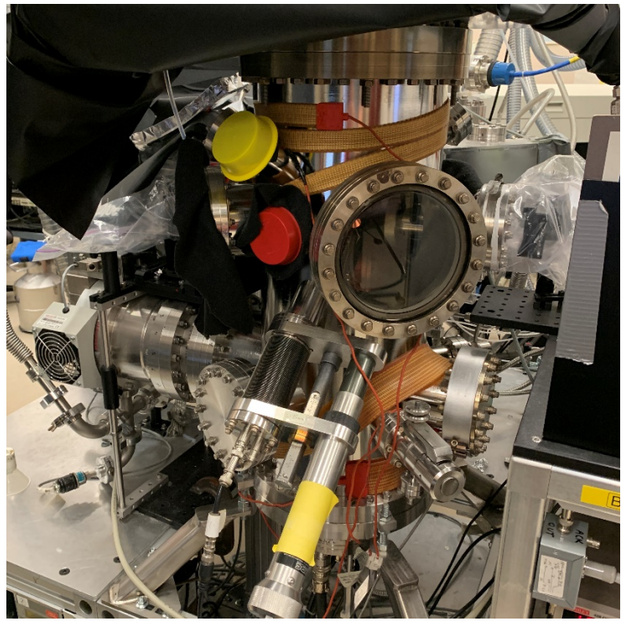


Shi, Russo, & Tanaka *PNAS* **115**:9444 (2018).

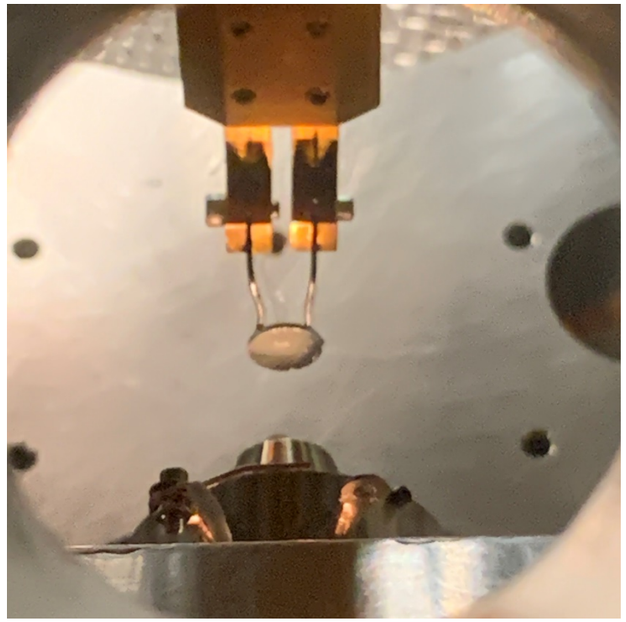
Russo, & Tanaka *Nat. Commun.* **5**:3556 (2014).

Studying water in the lab – the sample

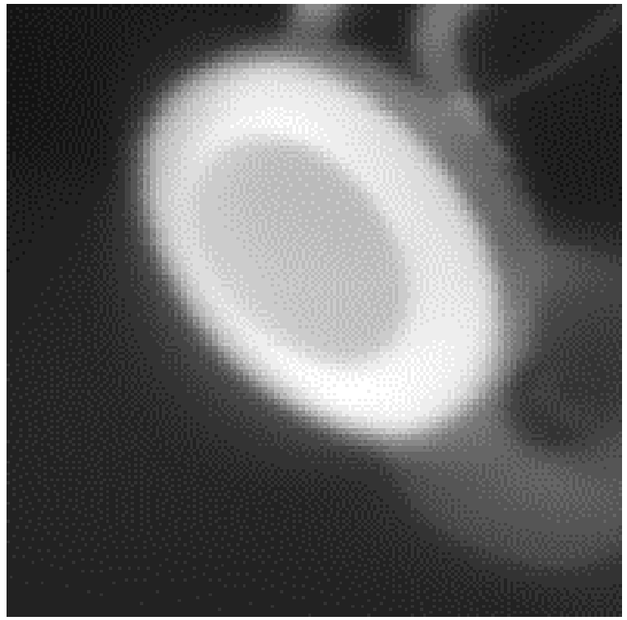
The Vacuum Chamber



Sample Holder



Adsorbed Water Sample



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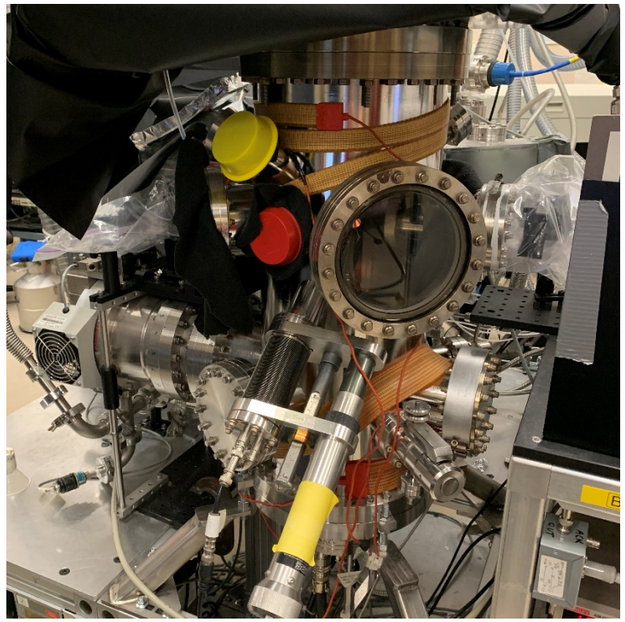
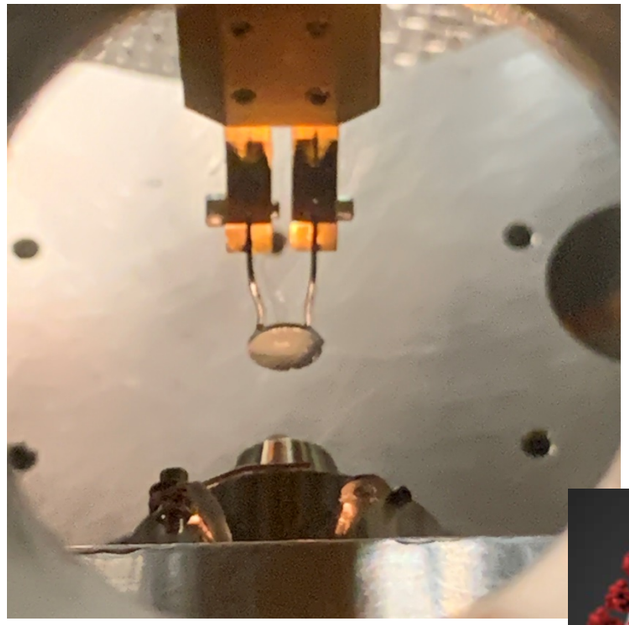


Sample Holder



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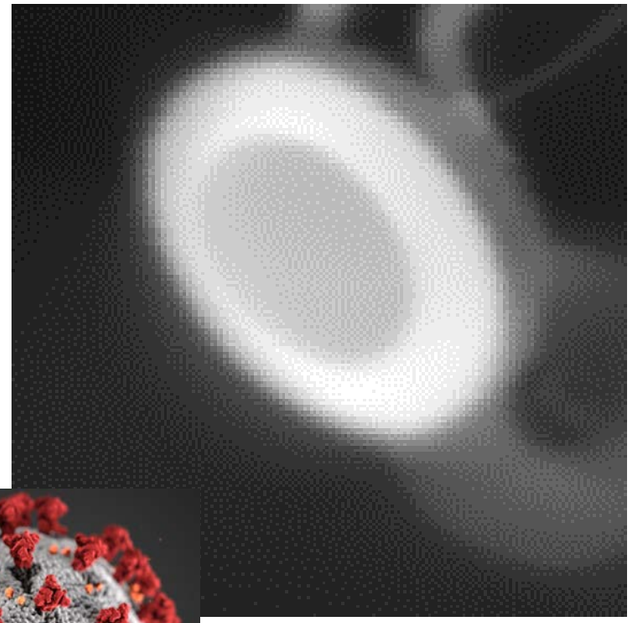
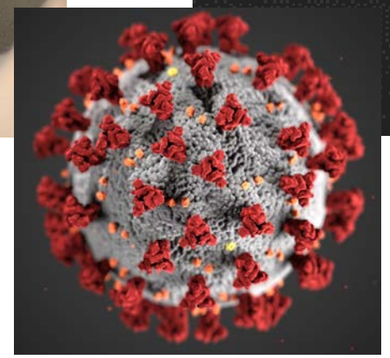
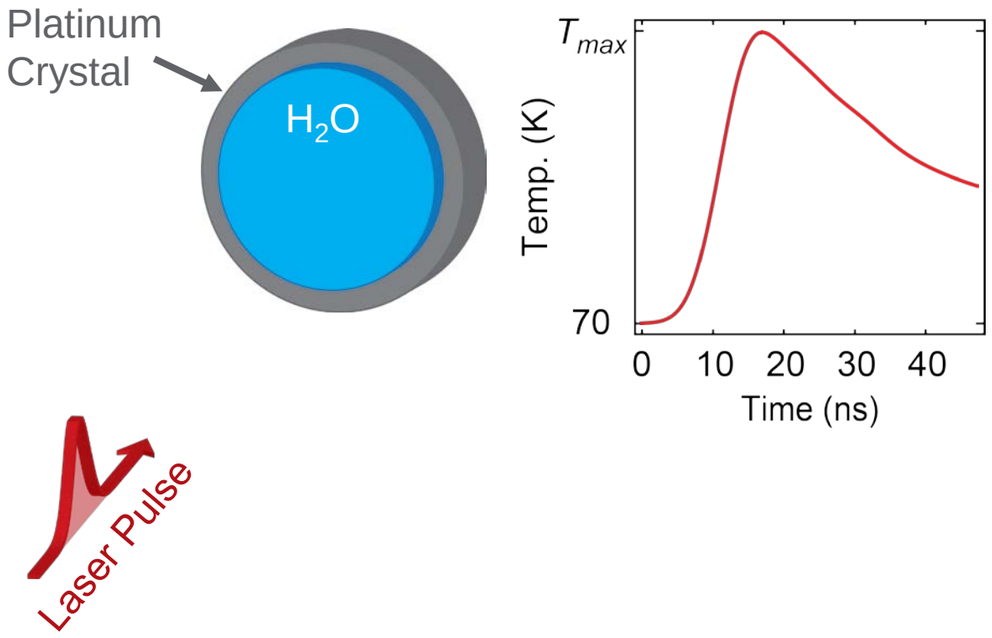




For scale:
Length coronavirus spike (red) is ~10 nm

Studying water in the lab – pulsed laser heating

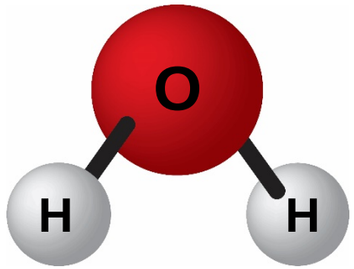


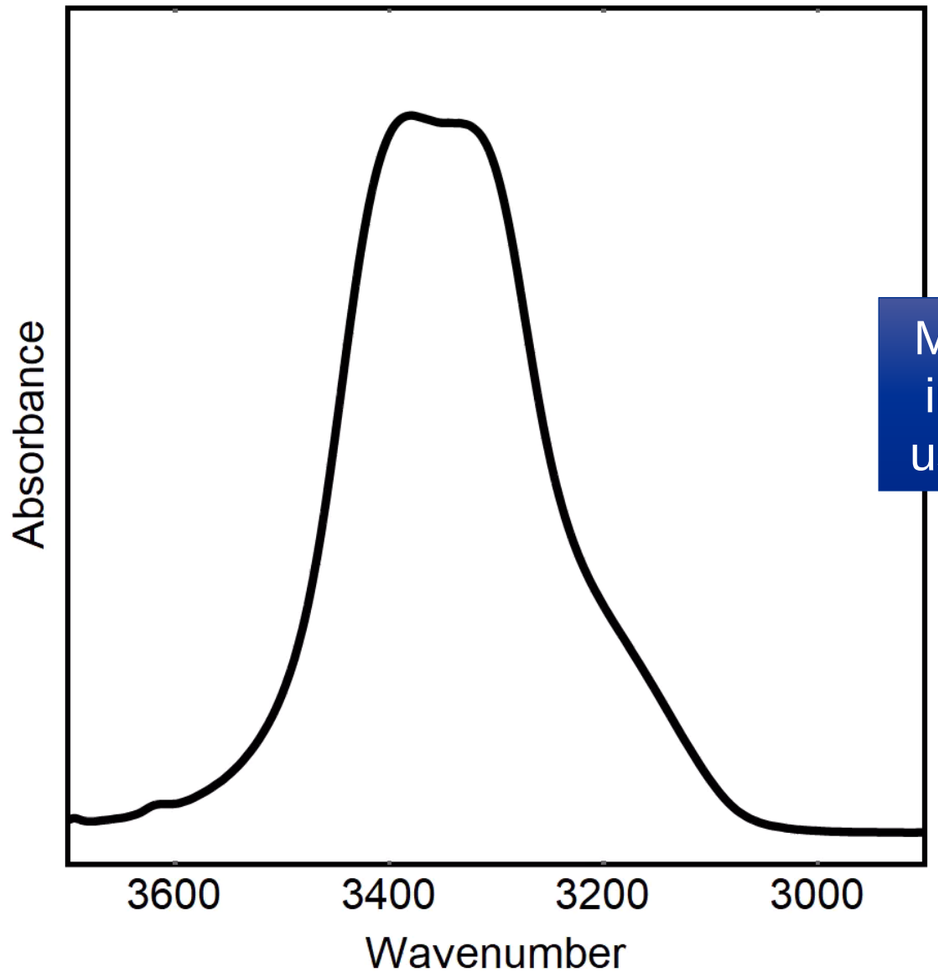
Technical Specs

- Maximum temperature (T_{max}) between 170 and 300 K (-154 and 80°F)
- Heating rate ~ 1×10^{10} K/s
- Cooling rate ~ 5×10^{9} K/s
- Collect IR spectra after a set number of pulses N_p
- All spectra are taken at 70 K

Xu et al. *J. Chem. Phys.* **144**:164201 (2016).

“Stop-motion” movie of chemical processes





Monitor structural changes, in nanosecond time steps, using infrared spectroscopy

Pacific Northwest
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Previously, the group used pulsed heating to study the crystallization process

THE JOURNAL OF CHEMICAL PHYSICS **144**, 164201 (2016)

A nanosecond pulsed laser heating system for studying liquid and supercooled liquid films in ultrahigh vacuum

Yuntao Xu,[a)] Collin J. Dibble,[a)] Nikolay G. Petrik, R. Scott Smith, Alan G. Joly, Russell G. Tonkyn, Bruce D. Kay,[b)] and Greg A. Kimmel[b)]
Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, USA

Growth rate of crystalline ice and the diffusivity of supercooled water from 126 to 262 K

Yuntao Xu[a], Nikolay G. Petrik[a], R. Scott Smith[a], Bruce D. Kay[a,1], and Greg A. Kimmel[a,1]

[a]Chemical Physics & Analysis, Physical Sciences Division, Physical & Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352

The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

Homogeneous ice nucleation rates and crystallization kinetics in transiently-heated, supercooled water films from 188 K to 230 K

Cite as: J. Chem. Phys. 150, 204509 (2019); doi: 10.1063/1.5100147
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Published Online: 31 May 2019

Greg A. Kimmel,[a)] Yuntao Xu,[b)] Alexandra Brumberg,[c)] Nikolay G. Petrik, R. Scott Smith, and Bruce D. Kay[a)]

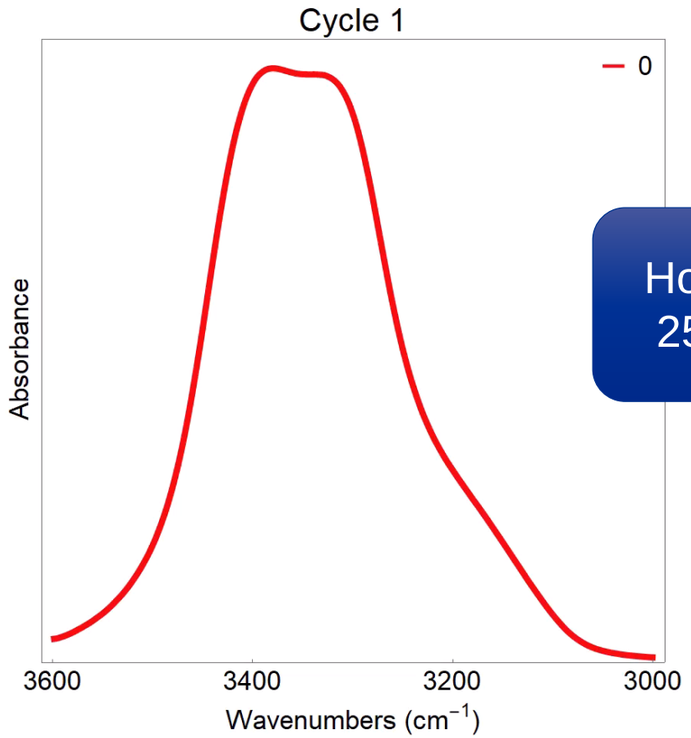
The Journal of Physical Chemistry Letters Letter
Cite This: J. Phys. Chem. Lett. 2017, 8, 5736-5743 pubs.acs.org/JPCL

Homogeneous Nucleation of Ice in Transiently-Heated, Supercooled Liquid Water Films

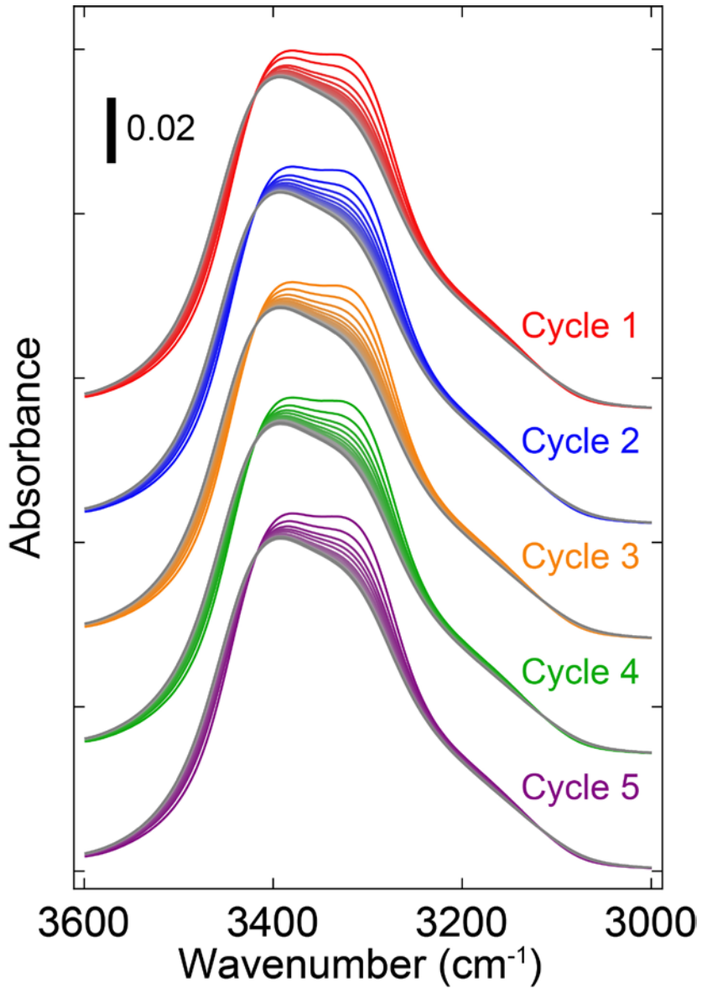
Yuntao Xu,[†] Nikolay G. Petrik, R. Scott Smith, Bruce D. Kay,[*] and Greg A. Kimmel[*]

Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, United States

Reversible transformations between a high and a low temperature structure



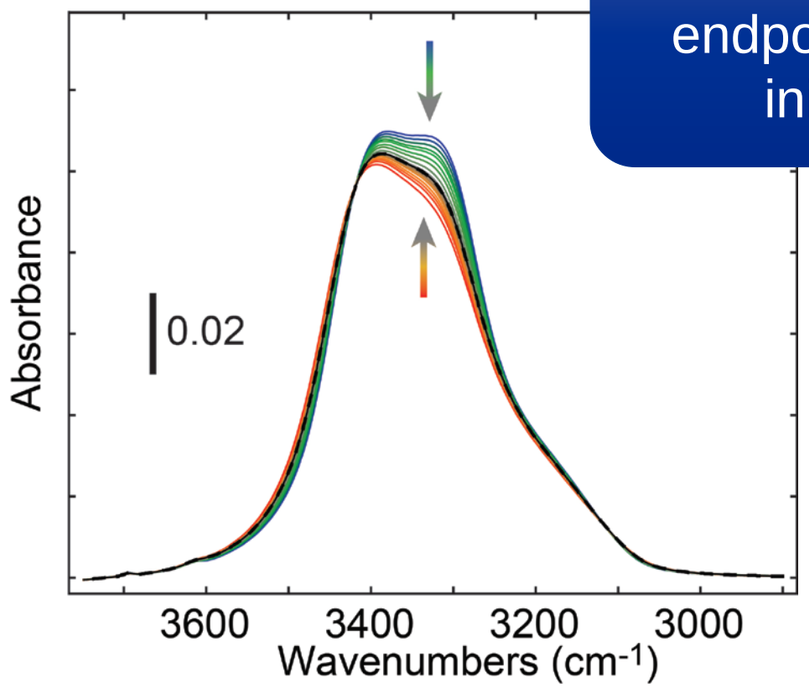
Hold at 135 K (-215°F) then
25 pulses at 241 K (-26°F)



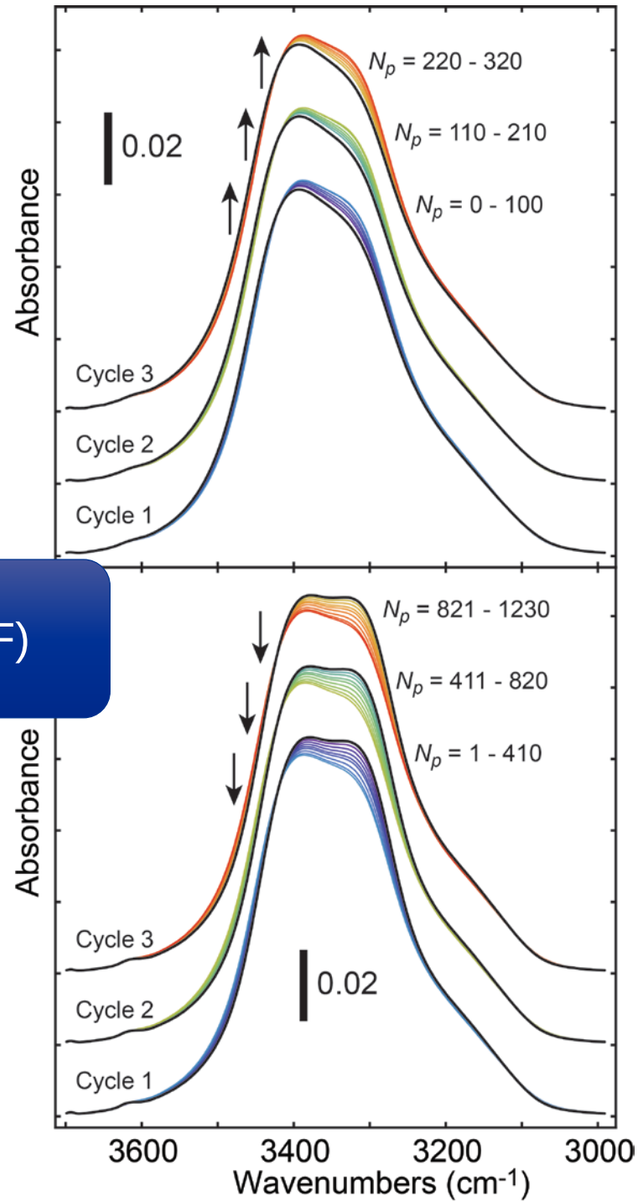
Kringle, Thornley, Kay, and Kimmel, *Science*, in press (2020).

Reversibility at temperatures in “No Man’s Land”

Intermediate temperature endpoint is independent of initial configuration

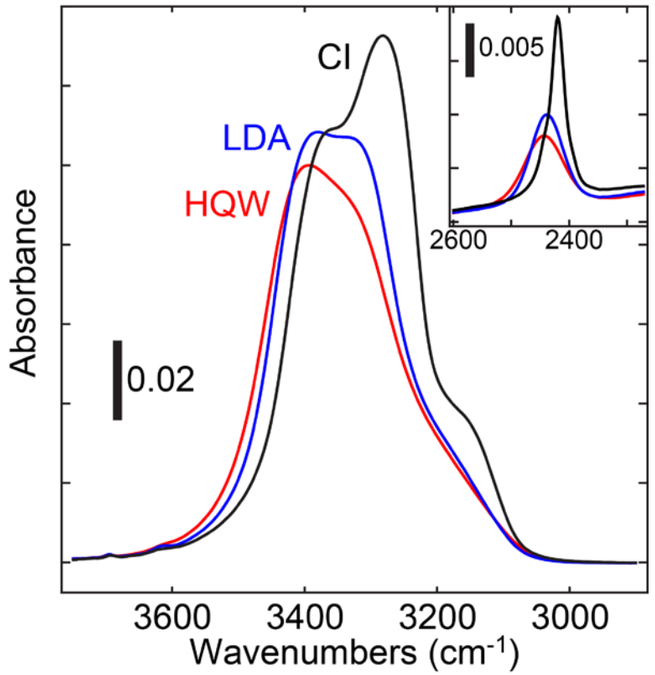


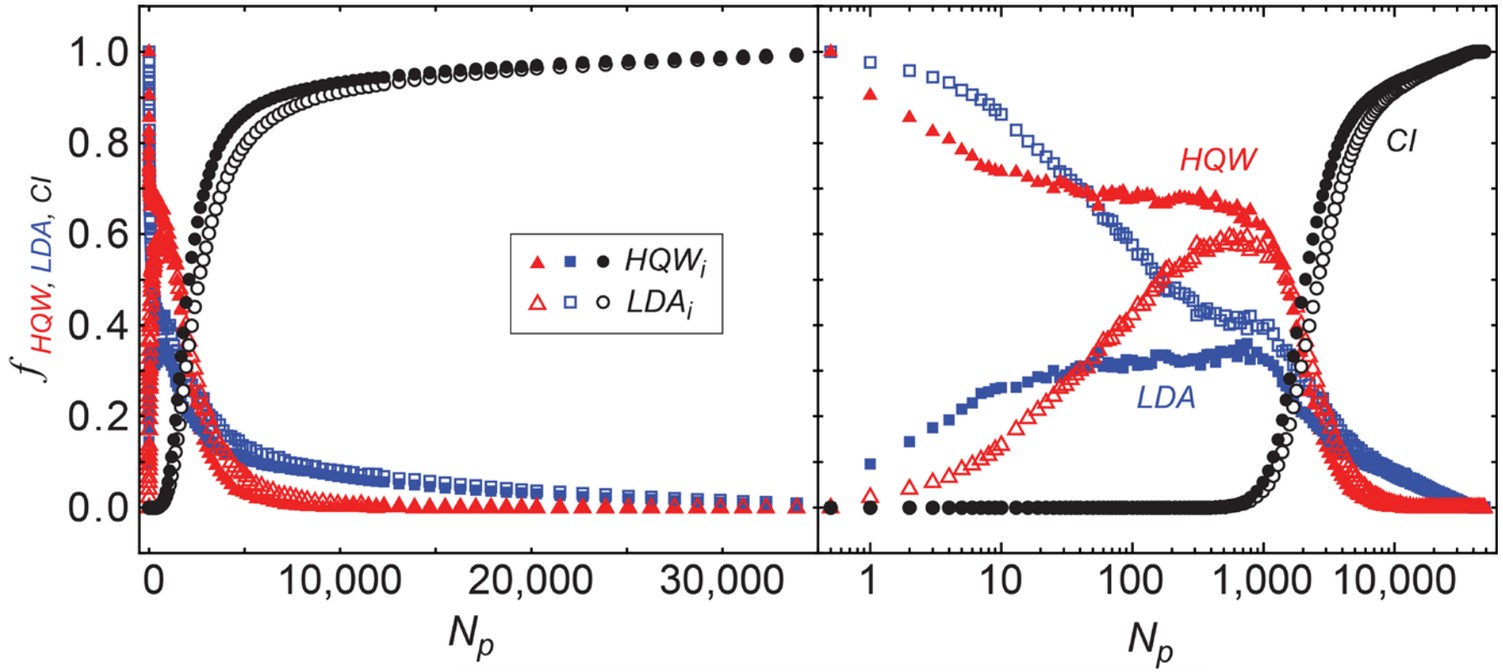
Cycles to 215 K (-73°F)



Kringle, Thornley, Kay, and Kimmel, *Science*, in press (2020).

Analyze the data as a combination of high-temperature, low-temperature, and crystalline

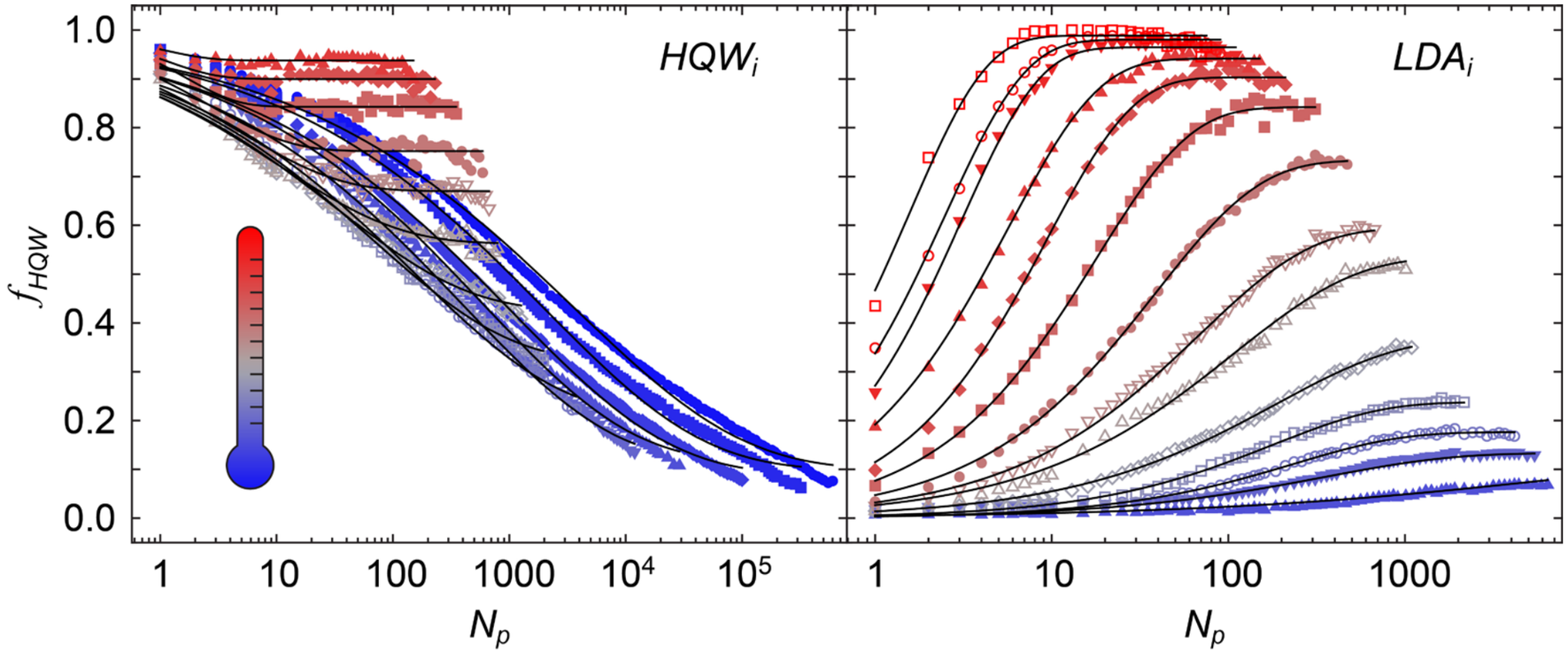




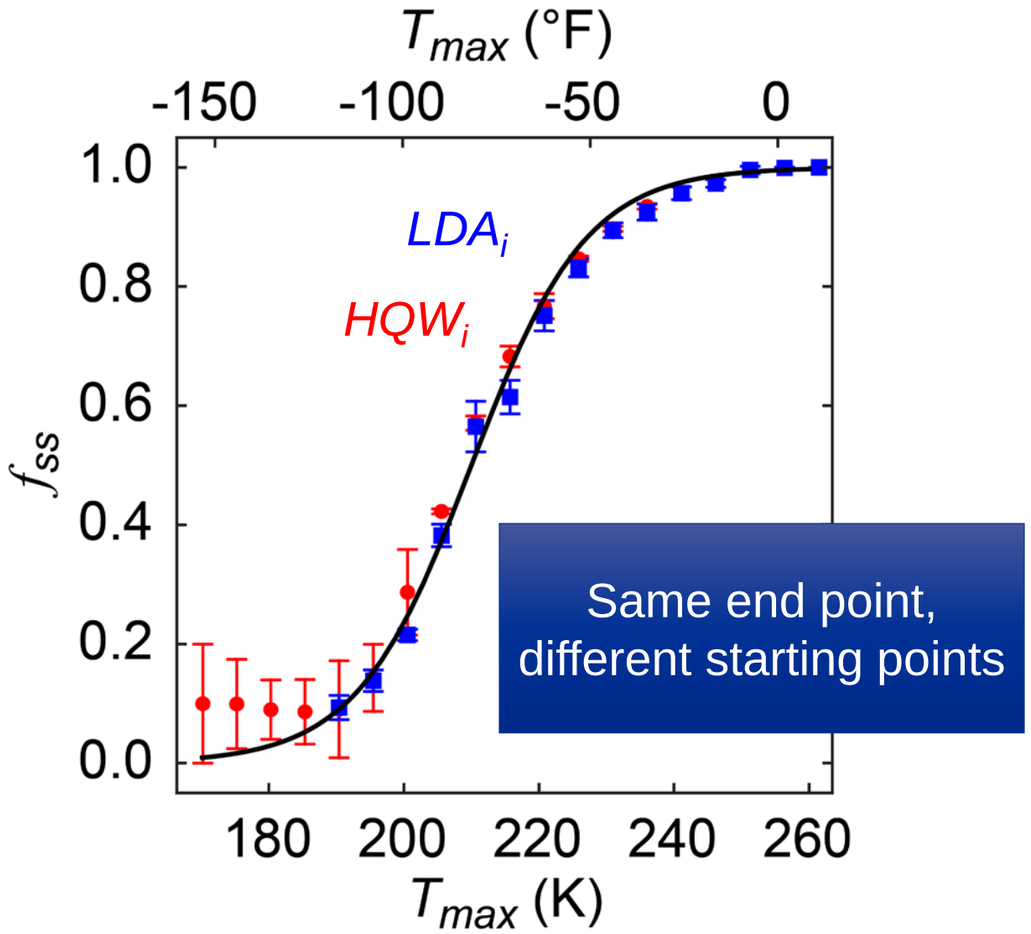
Eventually it will crystallize

Kringle, Thornley, Kay, and Kimmel, *Science*, in press (2020).

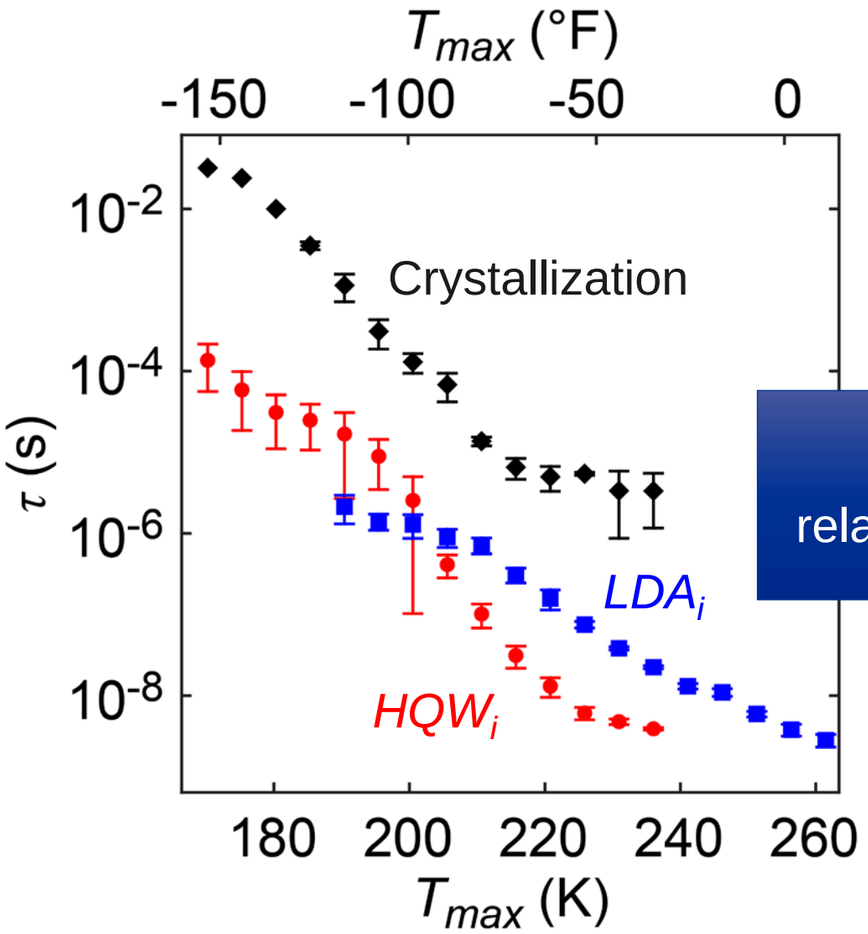
We measured water relaxation across “No Man’s Land”



Relaxation to a metastable state occurs before crystallization



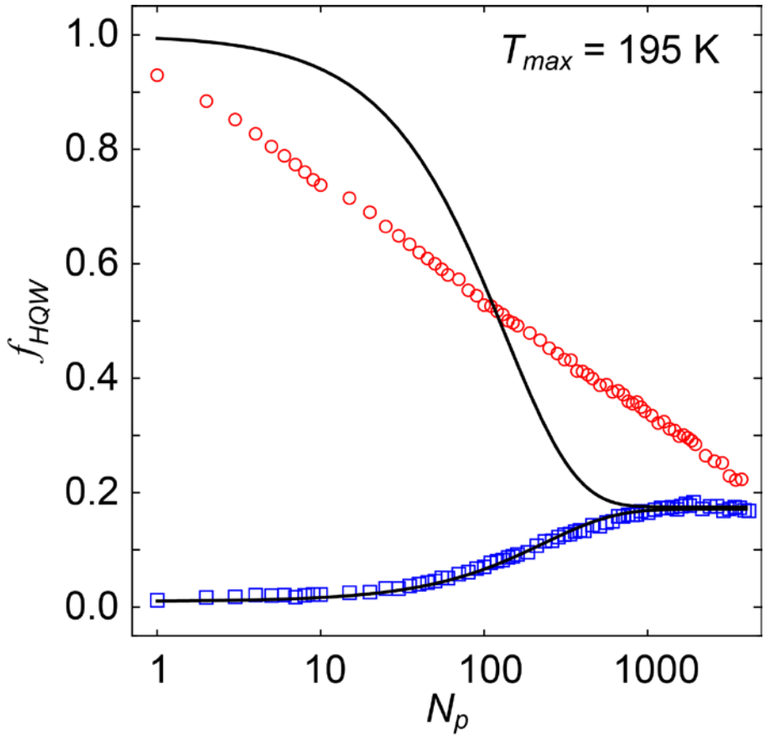
Same end point, different starting points

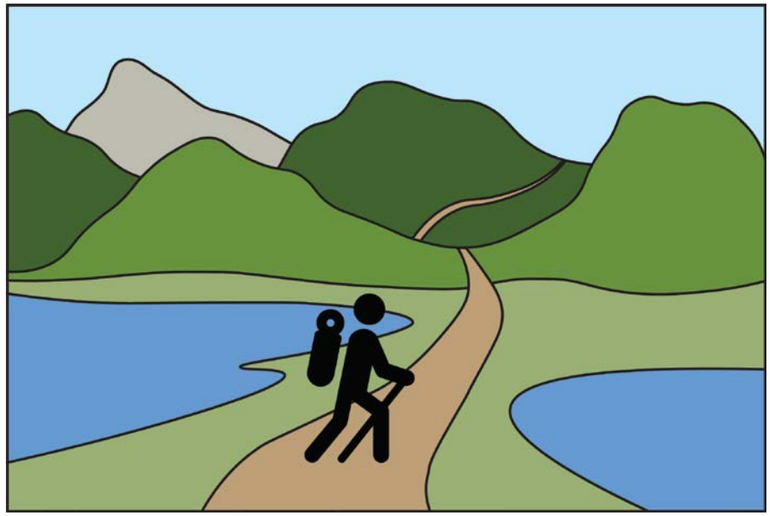


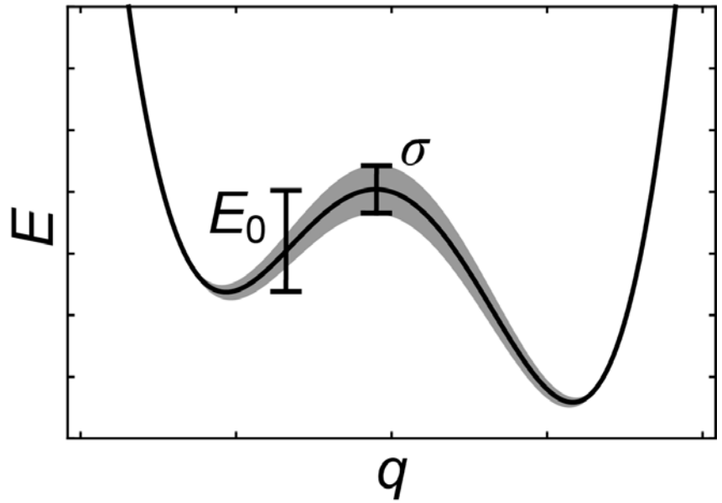
Different relaxation times

Kringle, Thornley, Kay, and Kimmel, *Science*, in press (2020).

Exploring a (potential energy) landscape





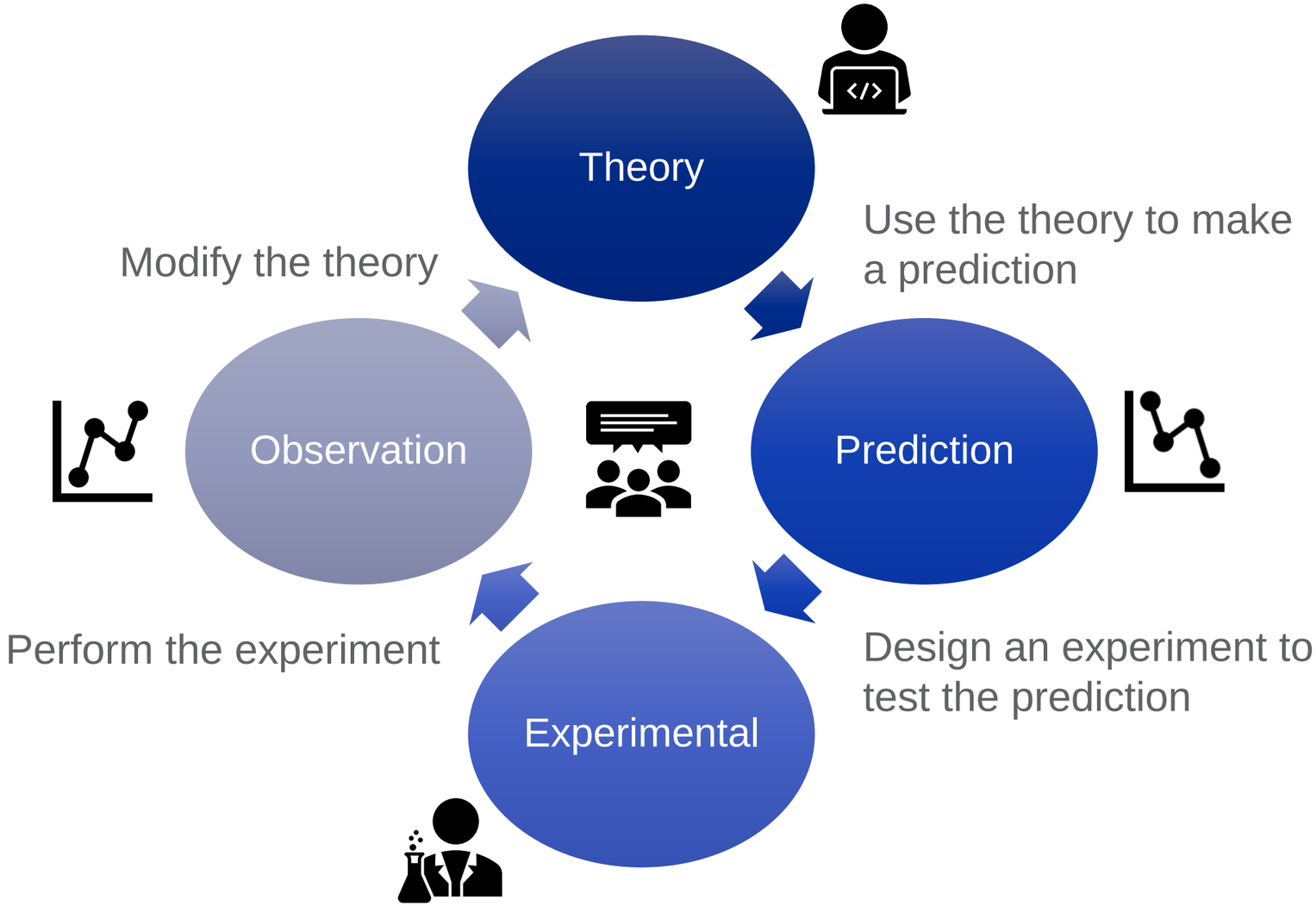


Two states and a distribution of activation energies

Conclusions

- Experimental examination of “No Man’s Land”
- Observed reversible structural transitions
- The supercooled liquid can be described by two structures
- Water reaches a metastable state before crystallization

What do these findings mean for the scientific community?



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