Glass Transition of Small Water Clusters

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雪、霧、水

Motivation

Amorphous ice

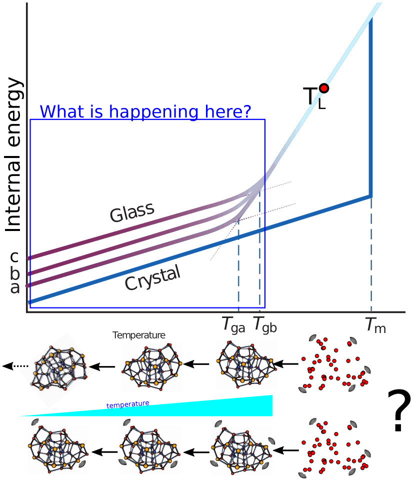
- the most abundant type of ice in the universe
- no molecular level studies
- small water clusters do not undergo crystallization

Main question

Do charged water clusters undergo a glass transition?

Sub-question

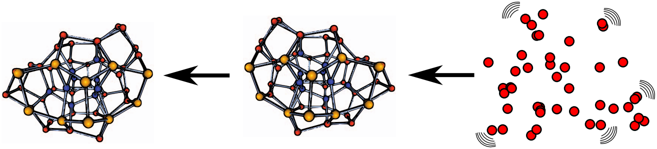
How many phase transitions do clusters undergo at temperatures < 100 K?



Proposal

Goal

Observation of structural transition of small charged water clusters $(H^+(H_2O)$ or $(H_2O)^-_{,}$ $n = 20$–200).



Means

RICE (Riken Cryogenic Electrostatic) storage ring

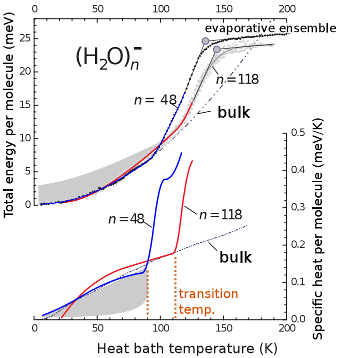
Methods

Photo-excitation and photo-fragmentation, mass and energy analysis of fragments, so called nano-calorimetry

The first-ever storage ring studies of water clusters!

What do we know so far

Thermal energy



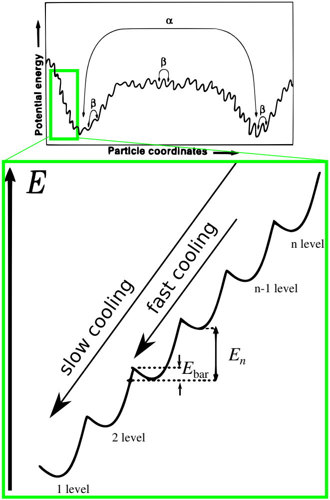
Heat capacity

Phys. Rev. Lett., 103, 073401 (2009)

- No sharp transition
- Sometimes unphysical low heat capacity

- Transition temperature varies with size
- and converges to glass transition of LDA ice for bulk.

Multistep cooling model



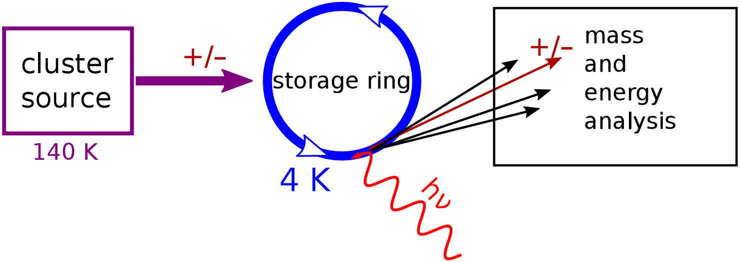
Stillinger F. H., Science 267, 1935 (1995)

- Fast cooling rate → high final internal energy, broad distribution of structural states
- Slow cooling rate → low internal energy, narrow distribution of structural states
- $E_{\mathrm{bar}} \sim 100\,\mathrm{meV}$ (Buck et al., PCCP 16, 6859, (2014))

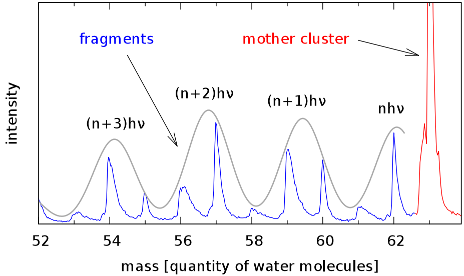
We would prefer having control over cooling process and final structural states.

Nobody has! However, we can in Riken.

Experiments in Riken



Fragment spectra for $(H_2O)_{63}^-$

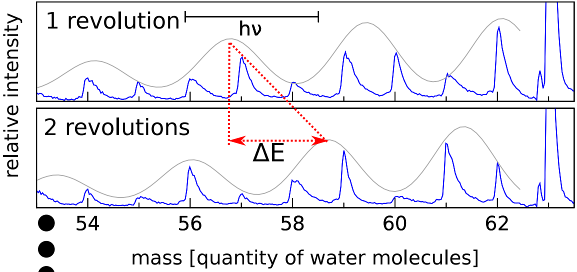


Radiative cooling is slow.

Only in this storage ring:

- No fragmentation caused by black body radiation from walls
- Detection of neutral fragments
- Any cluster size.

Nano-calorimetry



$$\Delta E = E_{i+1} - E_i$$

A skip in ΔE indicates the phase transition!

Other phase change indicators

- changes in vibrational spectra (hydrogen-bonded or free OH-stretching)
- changes in electron emission rate after laser irradiation (for $(H_2O)_n^-$)

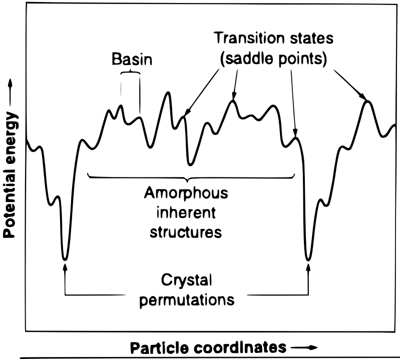
Other things to observe

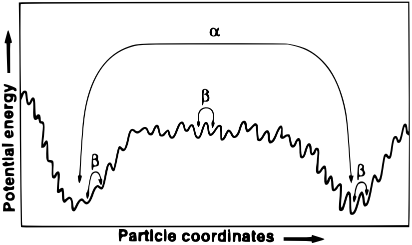
- Fragmentation dynamics
- Preferential fragmentation of isomers (pump-probe method)
- Annealing (irradiation by laser at the transition temperature)

etc.

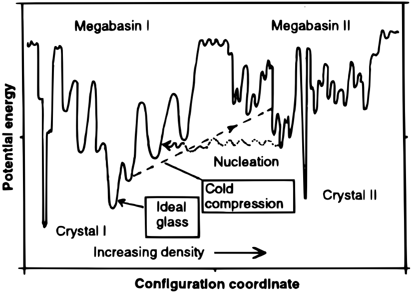
Thank you for your attention

Supplementary materials – potential profiles



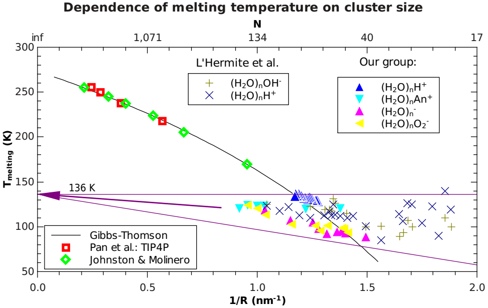


Stillinger F. H., Science 267, 1935 (1995)



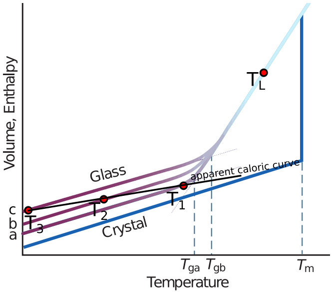
Angell C. A., Science 267, 1926 (1995)

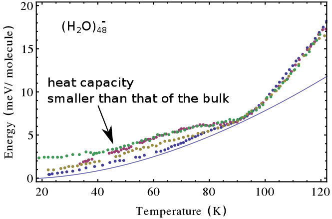
Supplementary materials – glass transition indications

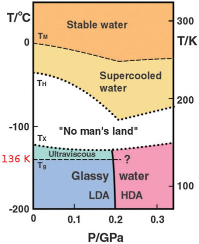


Julien Boulon, Isabelle Braud, Sébastien Zamith, Pierre Labastie, and Jean-Marc L'Hermite JCP 140, 164305 (2014)

M. Schmidt and B. von Issendorff, JCP 136, 164307 (2012)

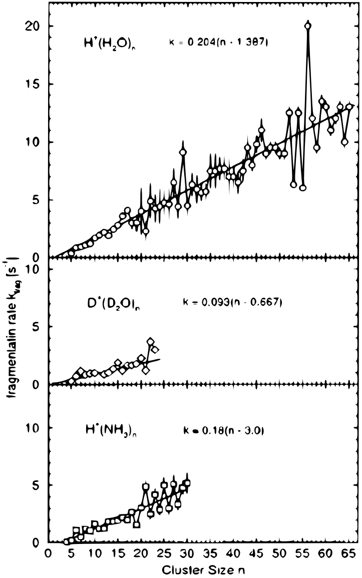






Loerting, PCCP 13, 8783 (2011)

Supplementary materials – rate of geometry change



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