Water: Decoding the percolation phase transition at 330 K with a nanoparticle ruler

CARLOS D. S. BRITES[1], BILIN ZHUANG[2,3], MENGISTIE L. DEBASU[1,4], DING DING[5], XIAN QIN[6], FERNANDO E. MATURI[1], WINNIE W. Y. LIM[2], DE WEN SOH[2], J. ROCHA[4], ZHIGAO YI[6], XIAOGANG LIU[6,7] & LUÍS D. CARLOS[1]

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The Journal of Physical Chemistry Letters

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Decoding a Percolation Phase Transition of Water at ∼330 K with a Nanoparticle Ruler

Carlos D. S. Brites,[▽] Bilin Zhuang,[*,▽] Mengistie L. Debasu, Ding Ding, Xian Qin, Fernando E. Maturi, Winnie W. Y. Lim, De Wen Soh, J. Rocha, Zhigao Yi, Xiaogang Liu,[*] and Luís D. Carlos[*]

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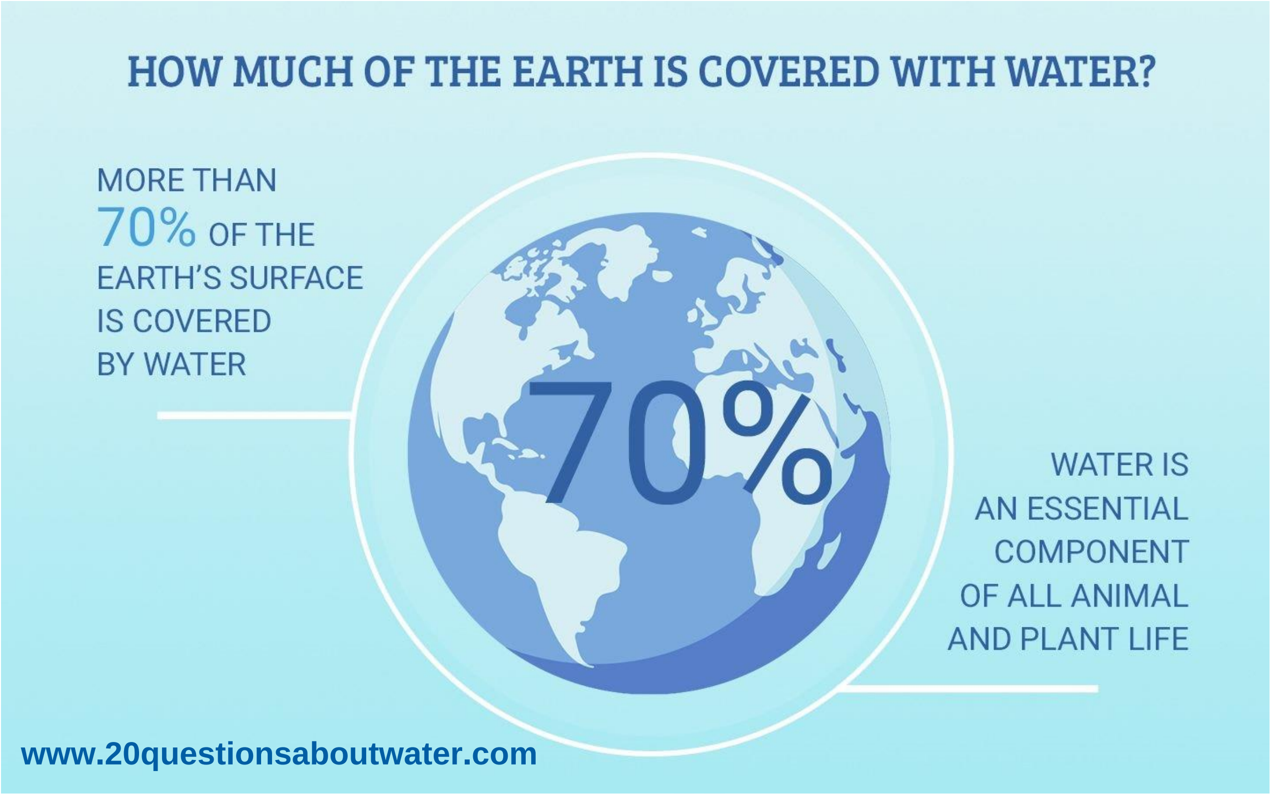
THE IMPORTANCE OF WATER

- Water is **the most important liquid for our existence** and plays an essential role in physics, chemistry, biology and geoscience.
- More than **70% of the earth's surface is covered by water**.

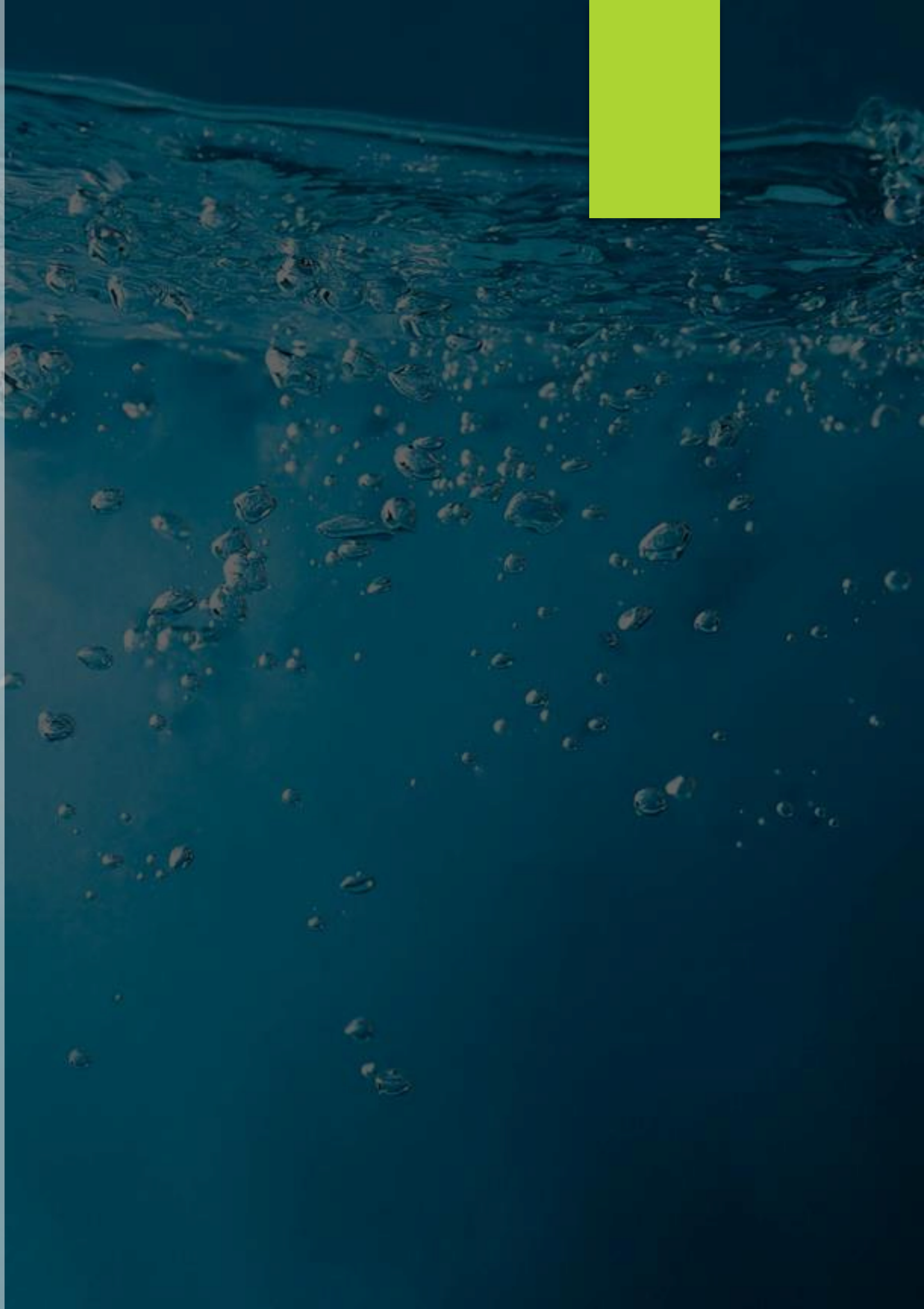


WATER ANOMALIES

- Water exhibits a **range of anomalous properties**
  - increased density upon melting, **density maximum at 277 K (4°C)**
  - reduced viscosity under pressure at below 306 K (33°C), high surface tension
  - decreased **isothermal compressibility (minimum at 319 K or 46°C)**
  - heat capacity with temperature at ambient conditions (minimum at 308 K or 35°C) respectively.

GOAL

use nanoparticles as rulers for accessing the transition between low- and high-density liquid water

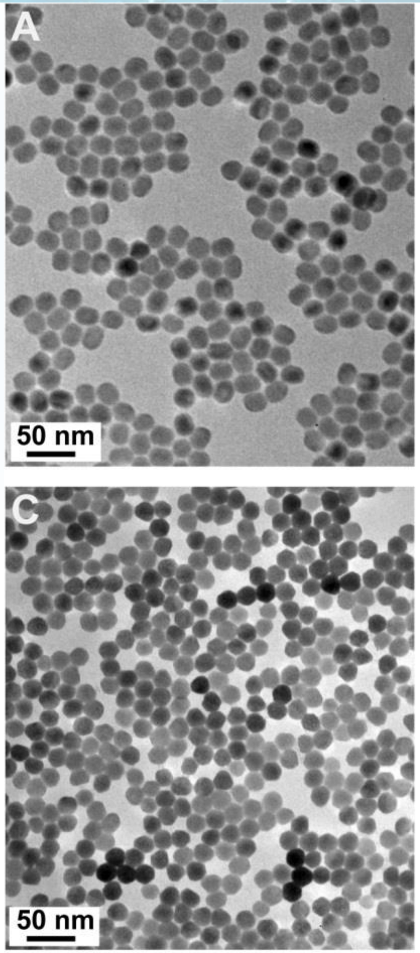


EXPERIMENTAL
Synthesis of the Nanoparticles

- Core-shell upconverting nanoparticles

$NaYF_4$:Yb/Er(18/2%)@$NaYF_4$ core-shell NPs (24 nm)

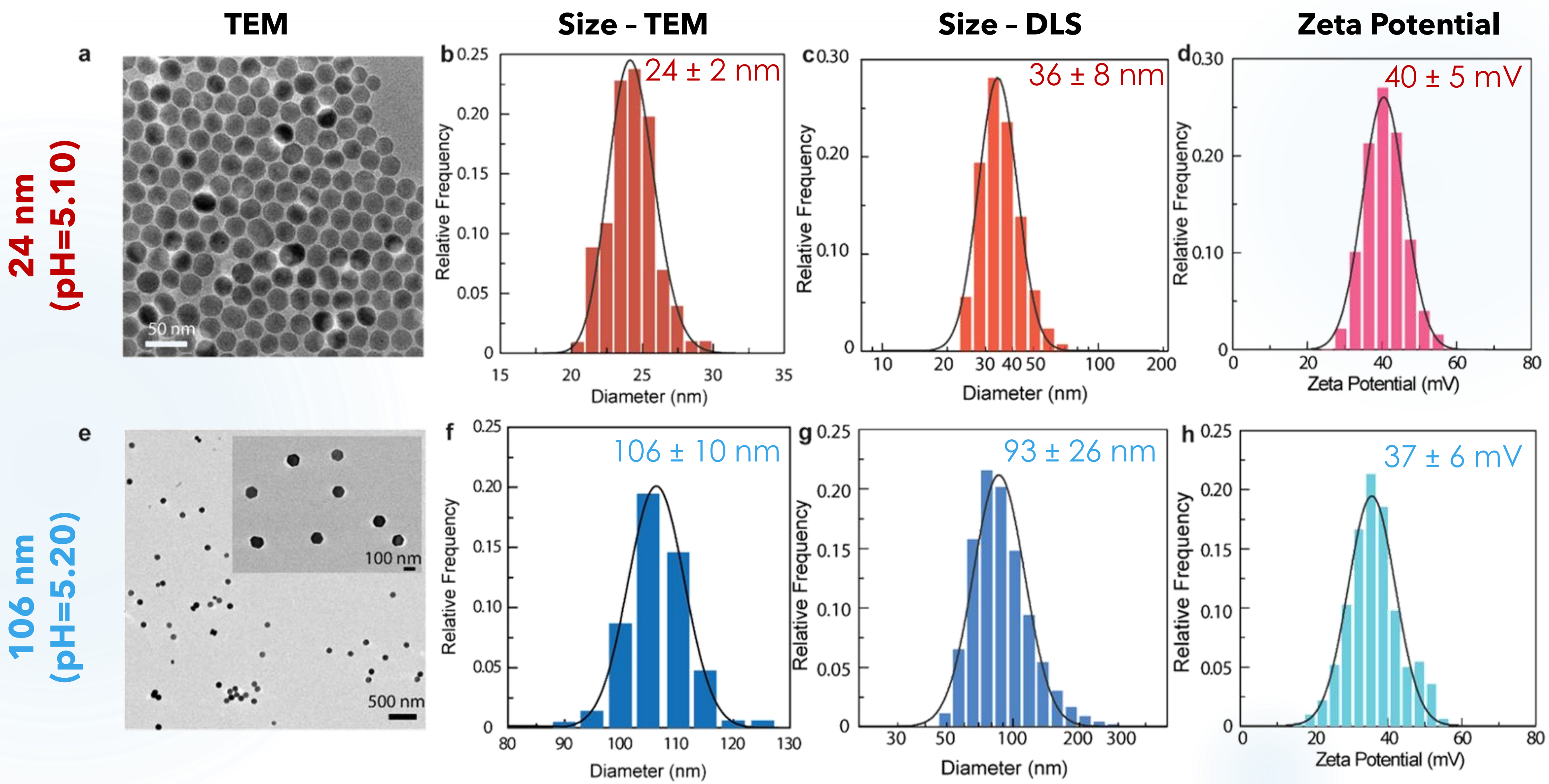
Ligand-free $NaYF_4$:Lu/Yb/Er (50/18/2%) nanoparticles (106 nm)



Nat. Nanotechnol. **11**, 851 (2016)

EXPERIMENTAL

Structural Characterization



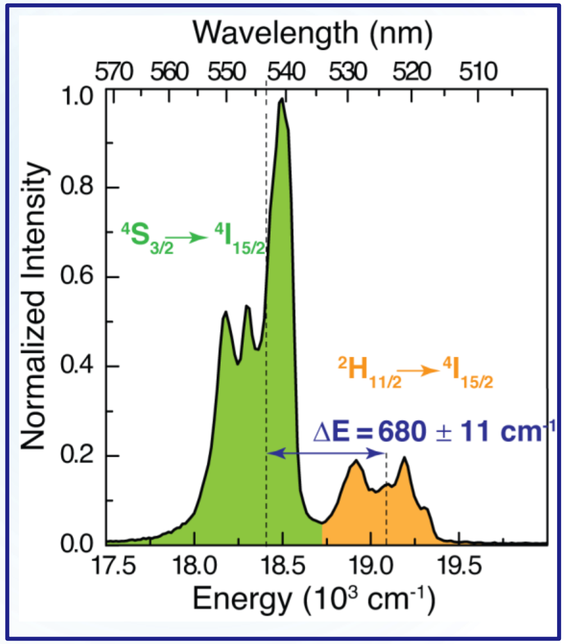
EXPERIMENTAL
Upconverting Thermometry

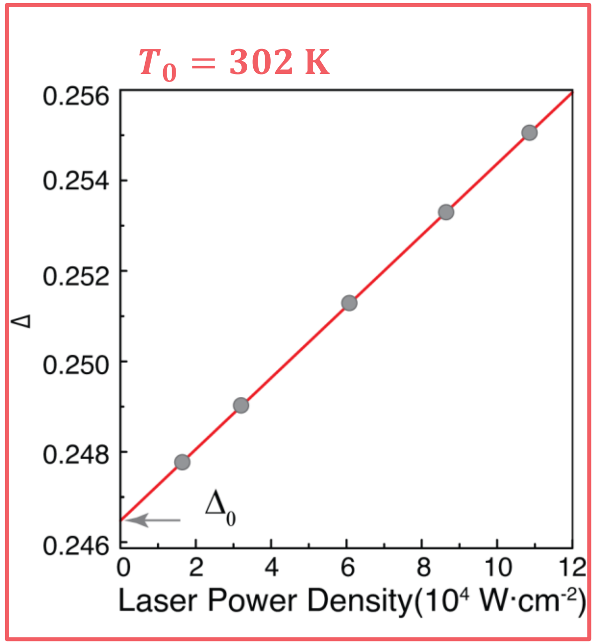


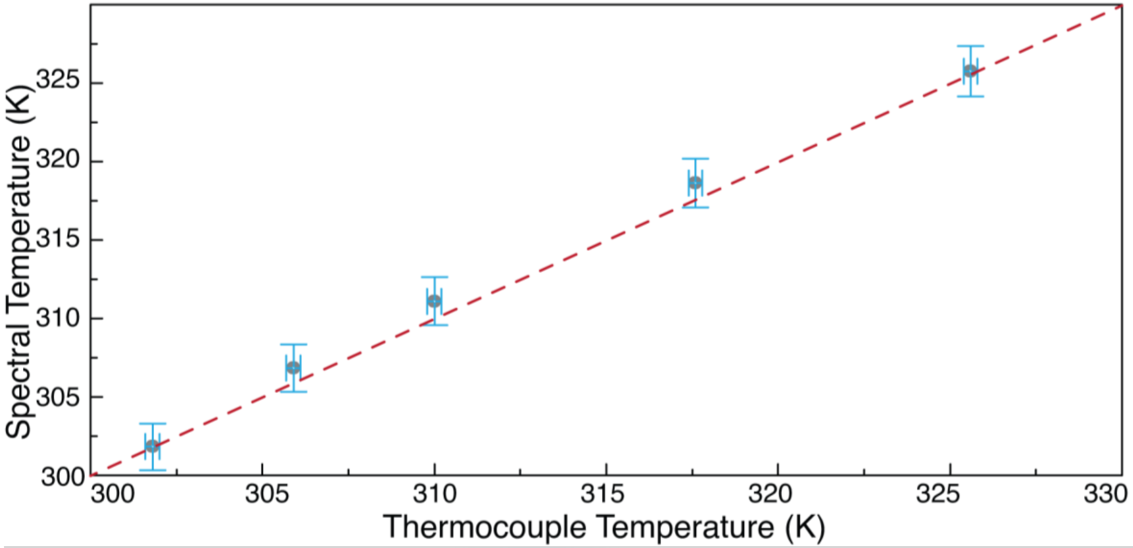
Fernando E. Maturi

$$\frac{1}{T} = \frac{1}{T_0} - \frac{k_B}{\Delta E}\ln\left(\frac{\Delta}{\Delta_0}\right)$$

24 nm (pH=5.10)



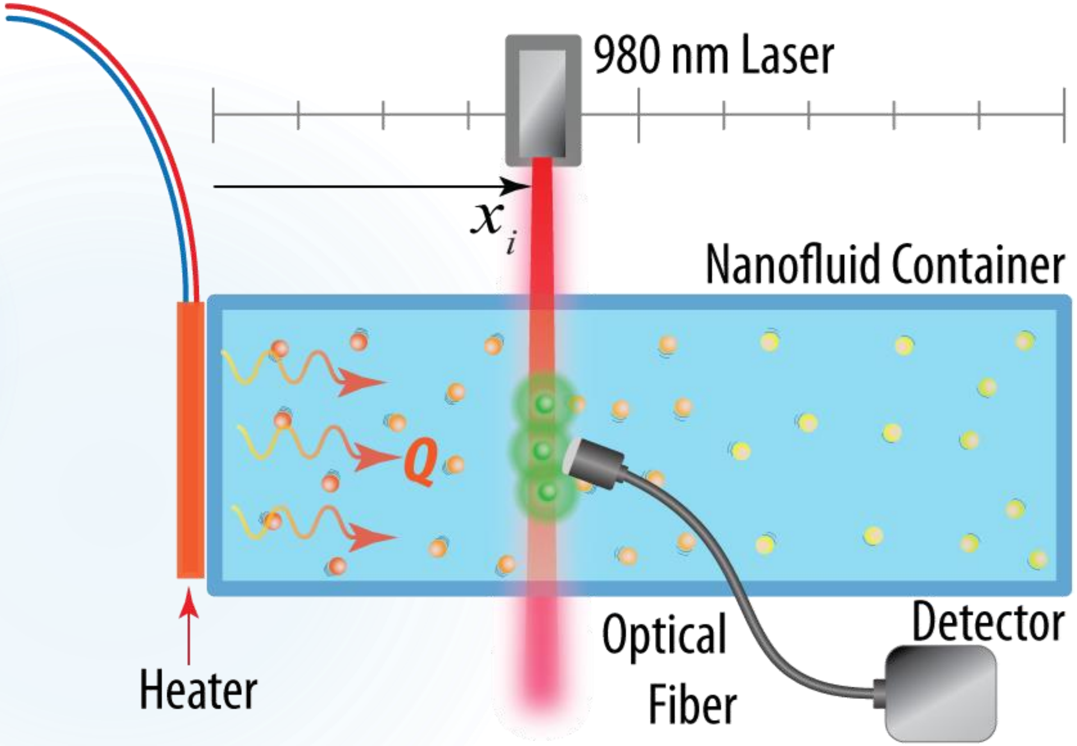


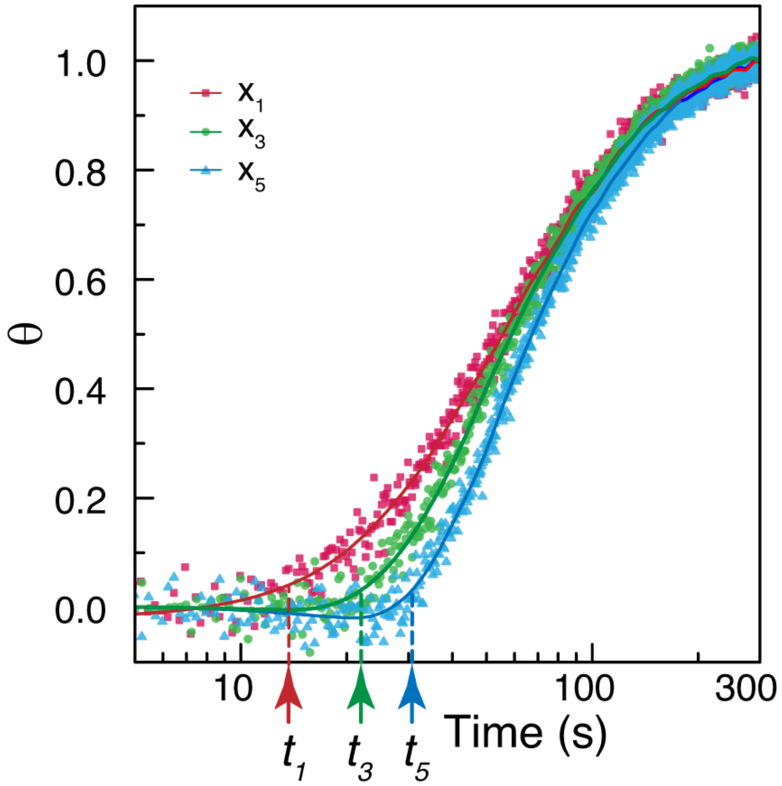


J. Phys. Chem. C **121**, 25, 13962 (2017)

EXPERIMENTAL

Accessing the Brownian Velocity



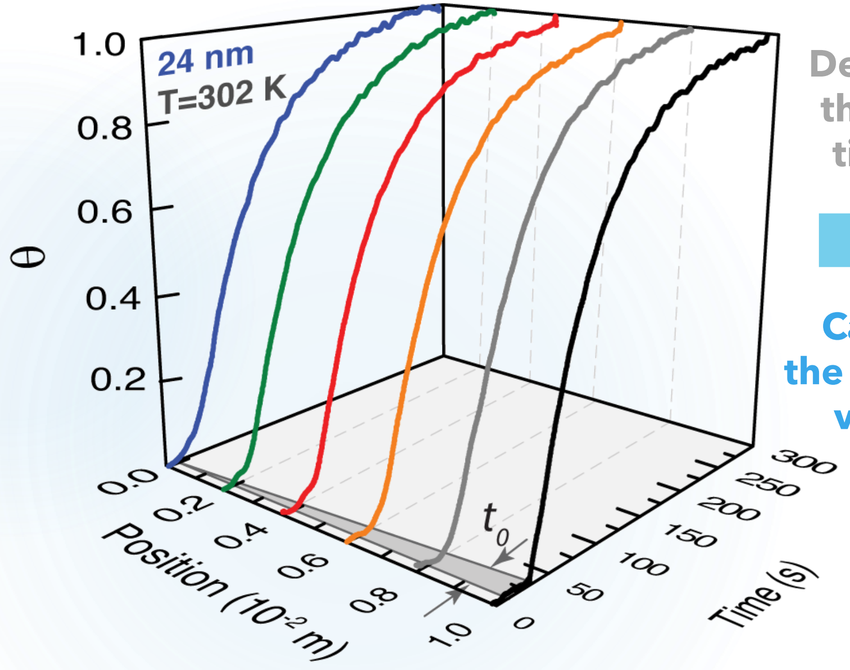


24 nm (pH=5.10)

Nat. Nanotechnol. **11**, 851 (2016)

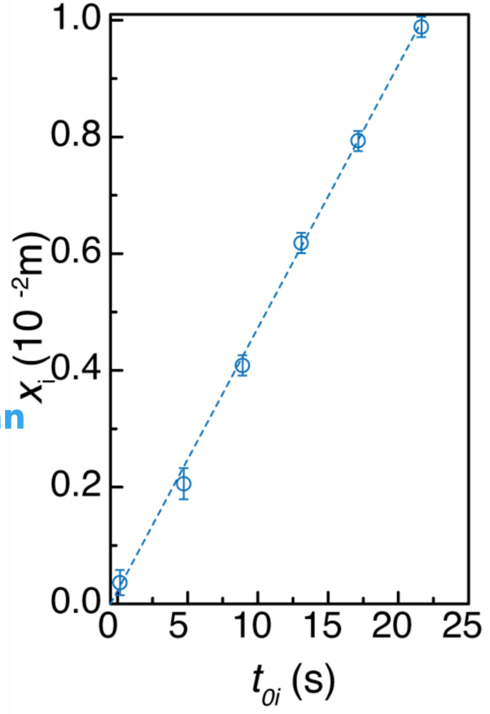
EXPERIMENTAL

Accessing the Brownian Velocity

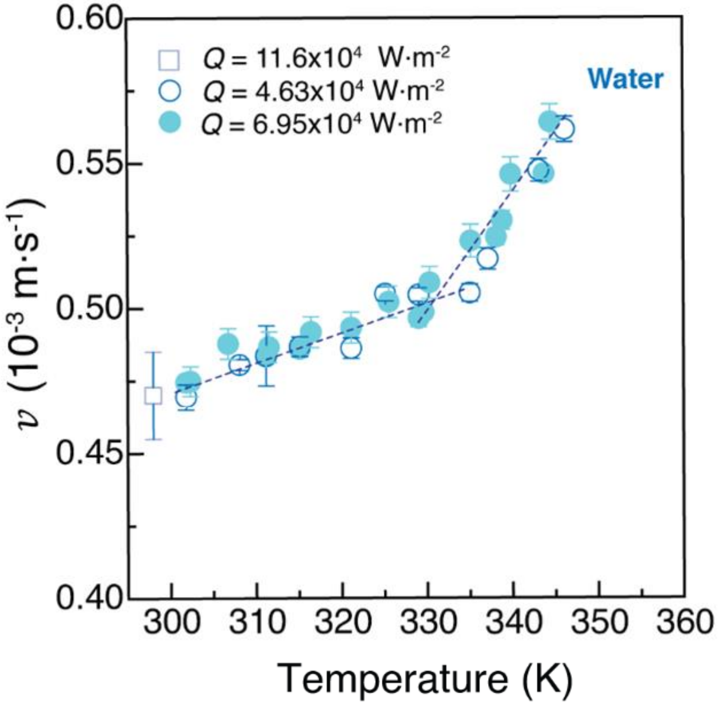


Determine the onset time (t_0)

Calculate the Brownian velocity



Scanning the initial solvent temperature



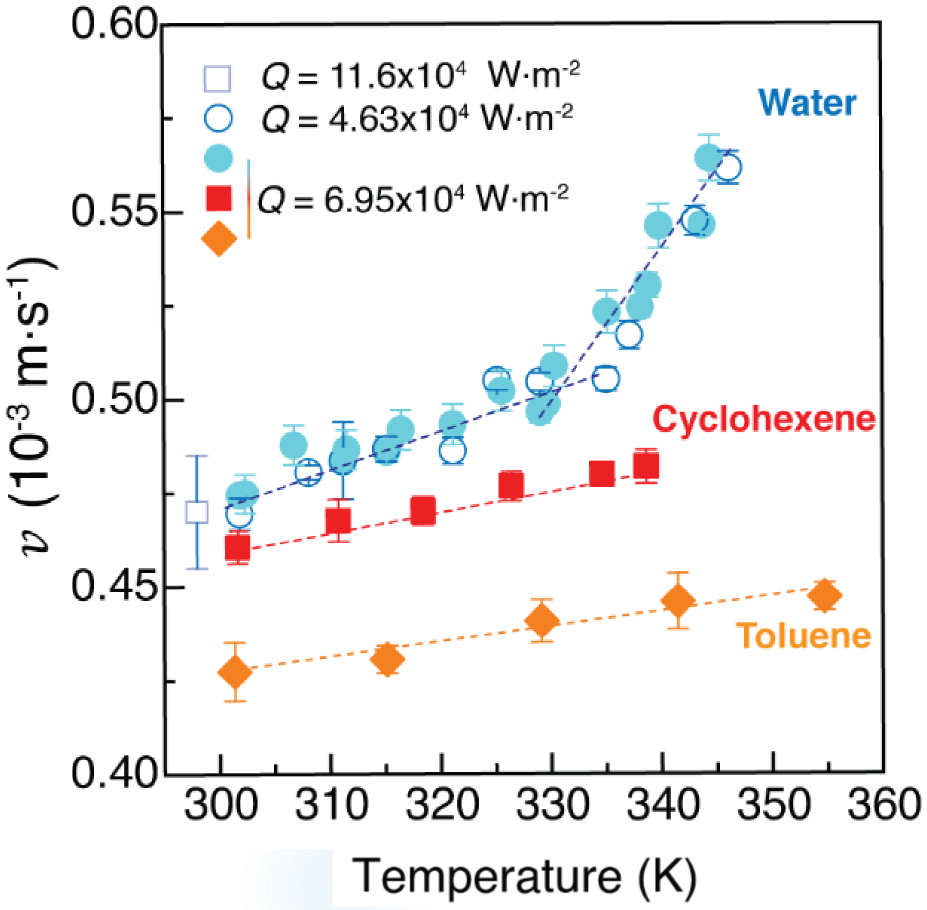
EXPERIMENTAL

Brownian Velocity in distinct solvents

- **Water** *vs* other organic solvents

  a clear and distinct bilinear behavior is clearly discerned in water, a clear signature near the **water's compressibility minimum**

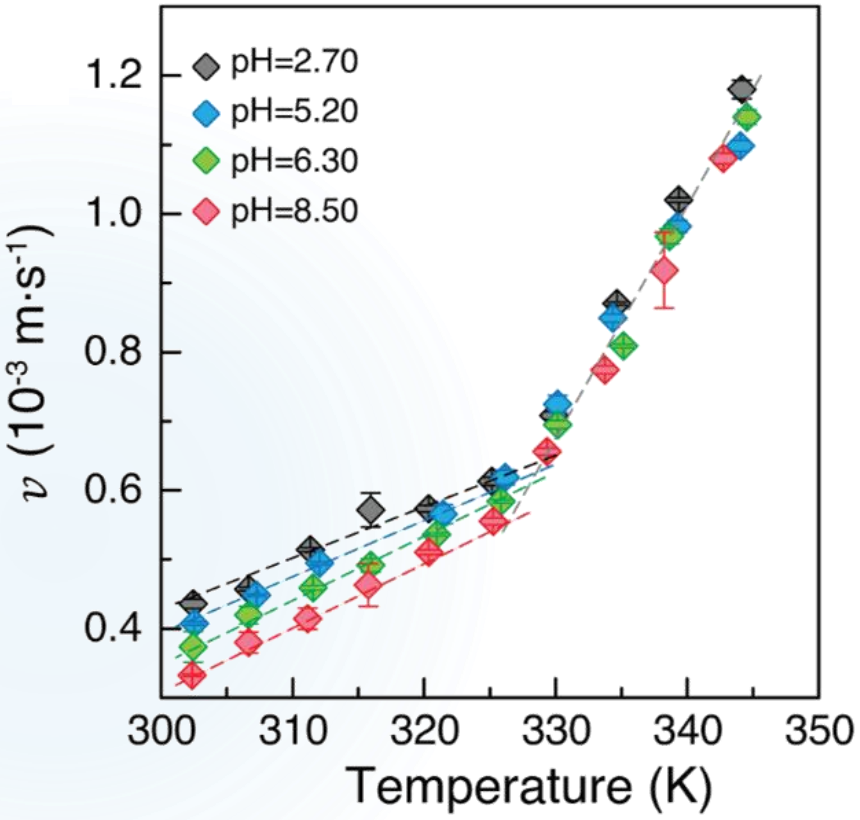
- A **crossover temperature** occurs in the transition between the two linear trends for water (irrespectively of the heating power employed)



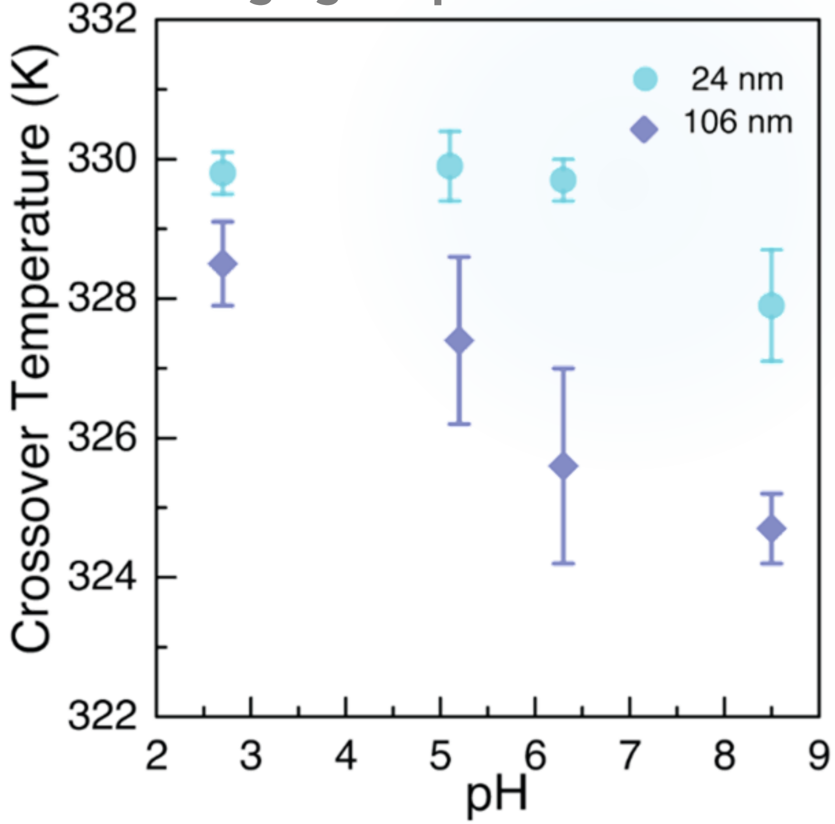
SCANNING THE WATER's compressibility minimum

Changing the pH value

106 nm (pH=5.20)



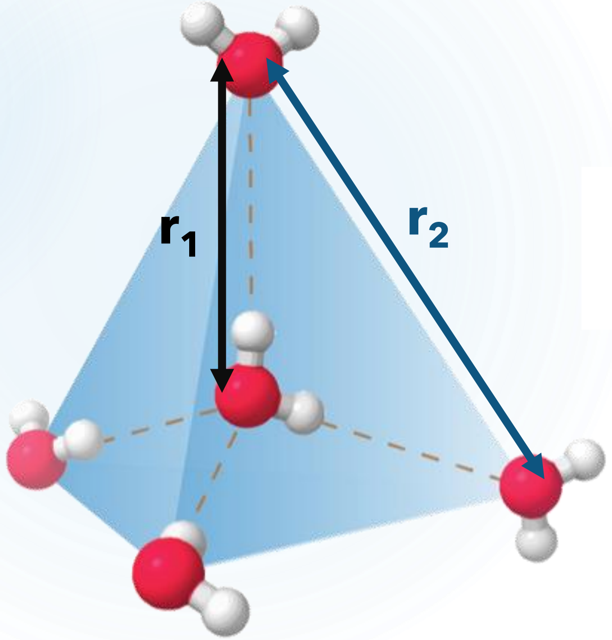
Changing the pH value / NP size

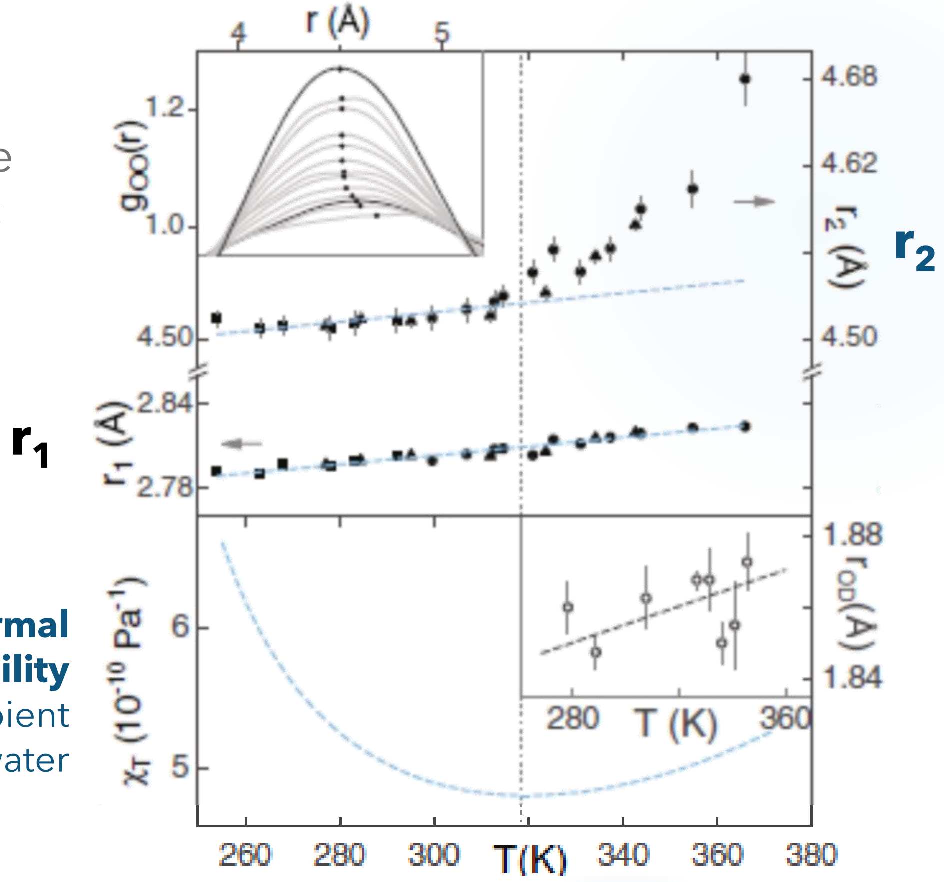


The bilinear behavior is clearly discerned in water, depending on the pH and NP size near the **water's compressibility minimum**

WATER's compressibility minimum
XRD results

The **water's tetrahedral** arrangement describes the structure of the liquid water at **lower temperatures**



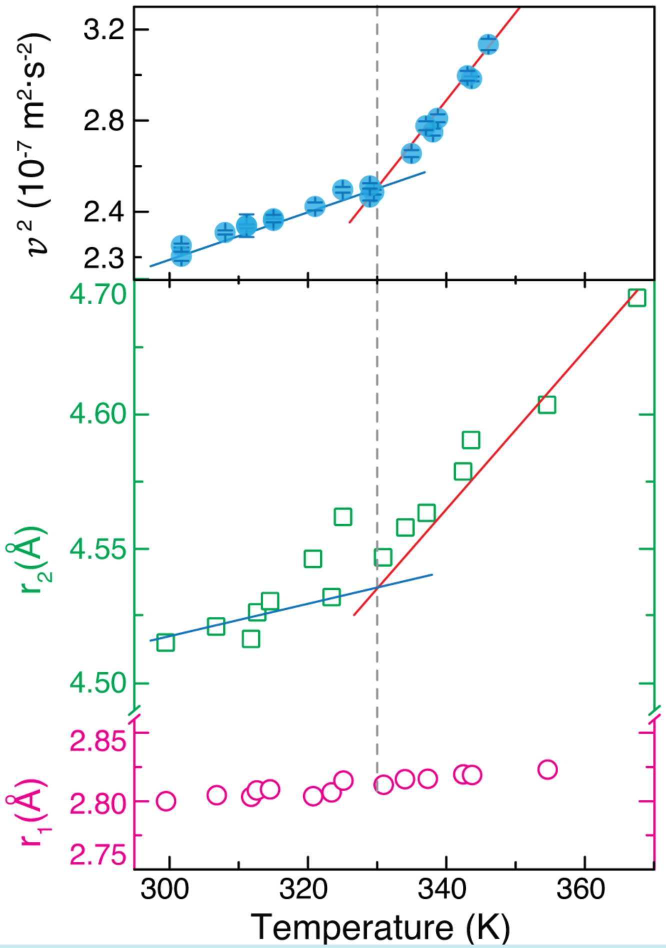


J. Chem. Phys. **141**, 214507 (2014)

WATER's compressibility minimum
our results

- The square of the **Brownian velocity presents a clear bilinear trend**. The **interception** of the two straight lines occurs **at a temperature (T_c)** about the temperature of the water's compressibility minimum

- The two-straight lines resemble those obtained using the same strategy on the structural XRD data reported by Skinner et al.



J. Chem. Phys. **141**, 214507 (2014)

Bilin Zhuang

Institute of High-Performance Computing
Yale-NUS College
Singapore

Rationalizing the observed changes in the **Brownian velocity** trough a percolating network of low- and high-density liquid water

LIQUID WATER is a mixture of two hydrogen-bonding structures

liquid water =

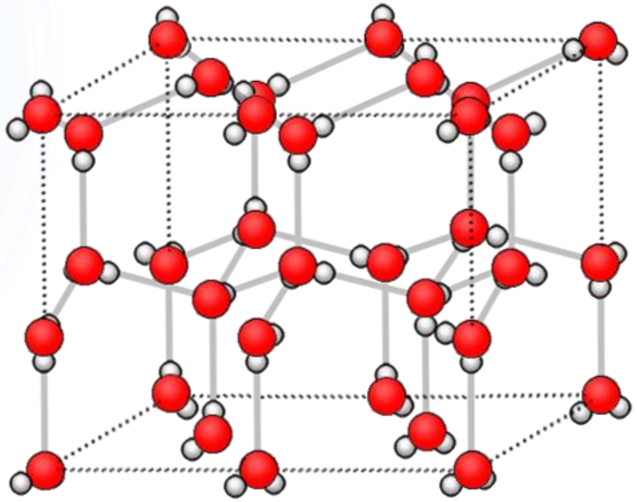
Less dense

favored at low temperature

+

More dense

favored at high temperature



Several recent references present a similar description for liquid water

RESEARCH

WATER STRUCTURE

Reversible structural transformations in supercooled liquid water from 135 to 245 K

Loni Kringle*, Wyatt A. Thornley*, Bruce D. Kay†, Greg A. Kimmel†

A fundamental understanding of the unusual properties of water remains elusive because of the limited data at the temperatures and pressures needed to decide among competing theories. We investigated the structural transformations of transiently heated supercooled water films, which evolved for several nanoseconds per pulse during fast laser heating before quenching to 70 kelvin (K). Water's structure relaxed from its initial configuration to a steady-state configuration before appreciable crystallization. Over the full temperature range investigated, all structural changes were reversible and reproducible by a linear combination of high- and low-temperature structural motifs. The fraction of the liquid with the high-temperature motif decreased rapidly as the temperature decreased from 245 to 190 K, consistent with the predictions of two-state "mixture" models for supercooled water in the supercritical regime.

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS Article

Direct Evidence in the Scattering Function for the Coexistence of Two Types of Local Structures in Liquid Water

Rui Shi and Hajime Tanaka*

Cite This: J. Am. Chem. Soc. 2020, 142, 2868–2875 Read Online

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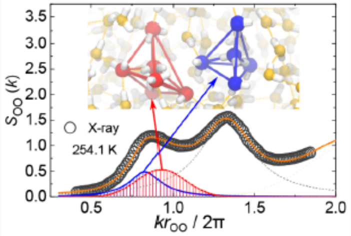
ABSTRACT: Water is the essential liquid on earth since it not only plays vital roles in living systems but also has a significant impact on our daily life from various industrial applications to earth's climate system. However, the unusual properties of liquid water, if compared with other liquids, has puzzled us for centuries because the basic structure of liquid water has remained unclear and has continued to be a matter of serious debate. Here, by computer simulations of three popular water models and the analysis of recent scattering experimental data, we show that there are two overlapped peaks hidden in the apparent "first diffraction peak" of the structure factor. One of them (ordinary peak) corresponds to the neighboring O–O distance as in ordinary liquids, and the other (anomalous peak) corresponds to a longer distance. We reveal that this anomalous peak arises from the most extended period of density wave associated with a tetrahedral water structure and is to be identified as the so-called first sharp diffraction peak that is commonly observed in silica and other tetrahedral liquids. In contrast, the ordinary peak arises from the density wave characteristic of local structures lacking tetrahedral symmetry. This finding unambiguously proves the coexistence of two types of local structures in liquid water. Our findings not only provide vital clues to settle a long-standing controversy on the water structure but also allow direct experimental access to the fraction of tetrahedral structures in liquid water.



Science **369** 1490 (2020)

JACS **142** 2868 (2020)

A percolation phase transition might explain our observations

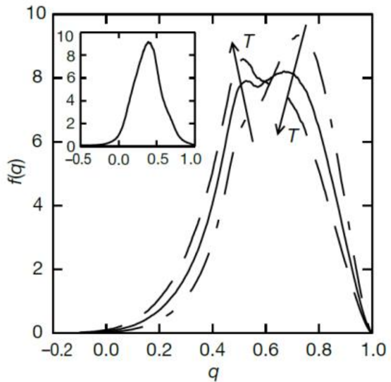
- A **percolation transition** occurs at the so called percolation threshold, which is the **point at which the microscopic elements become connected** for the first time, and **form a sample-spanning path** across the system

Relationship between structural order and the anomalies of liquid water

Jeffrey R. Errington & Pablo G. Debenedetti

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544-5263, USA

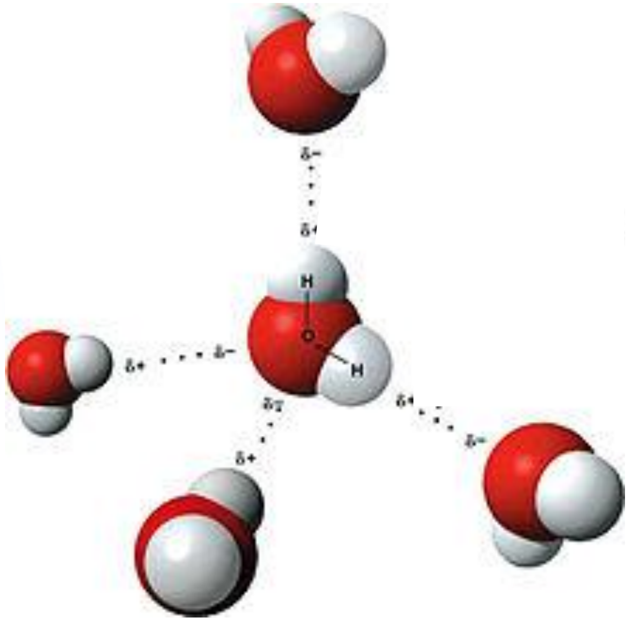
In contrast to crystalline solids—for which a precise framework exists for describing structure[1]—quantifying structural order in liquids and glasses has proved more difficult because even though such systems possess short-range order, they lack long-range crystalline order. Some progress has been made using model systems of hard spheres[2,3], but it remains difficult to describe accurately liquids such as water, where directional attractions (hydrogen bonds) combine with short-range repulsions to



Nature **409** 318 (2001)

Each molecule in water has different TETRAHEDRAL orientational order

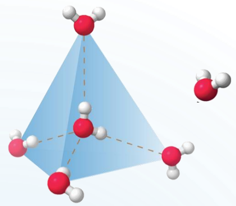
$$q = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\psi_{jk} + \frac{1}{3}\right)^2$$



Nature **409** 318 (2001)

A percolation phase transition might explain our observations

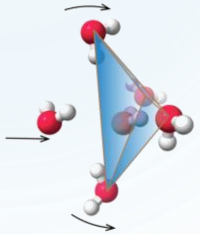
tetrahedral state (TH)



maximal tetrahedral order among the nearest four neighbors

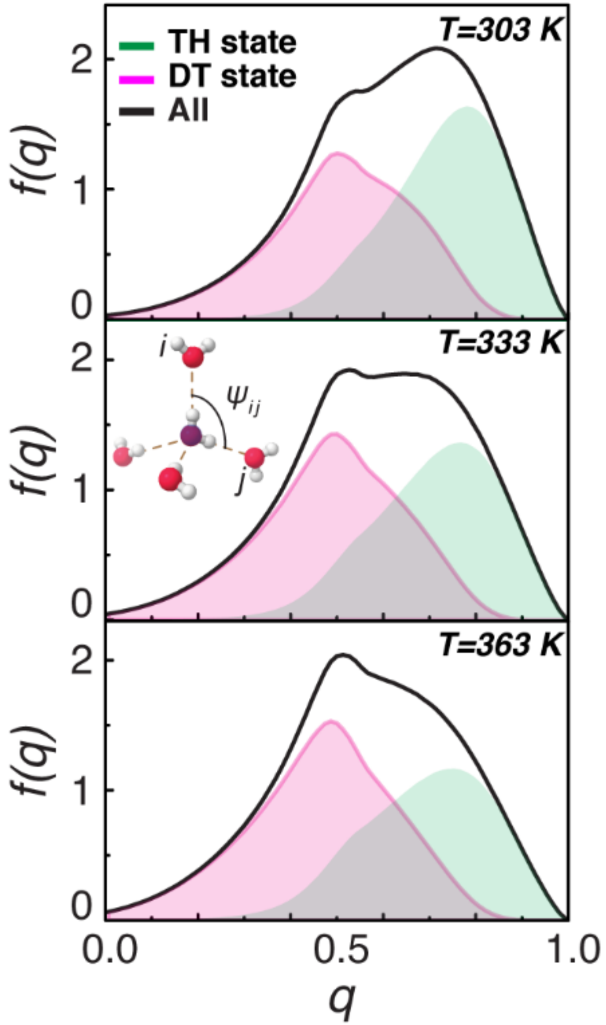
LOW DENSITY

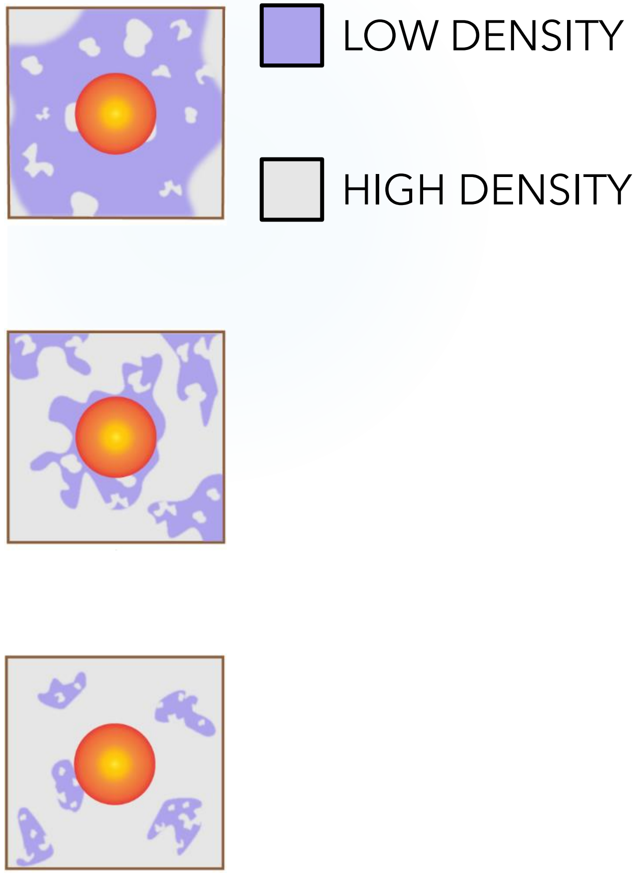
disrupted state (DT)



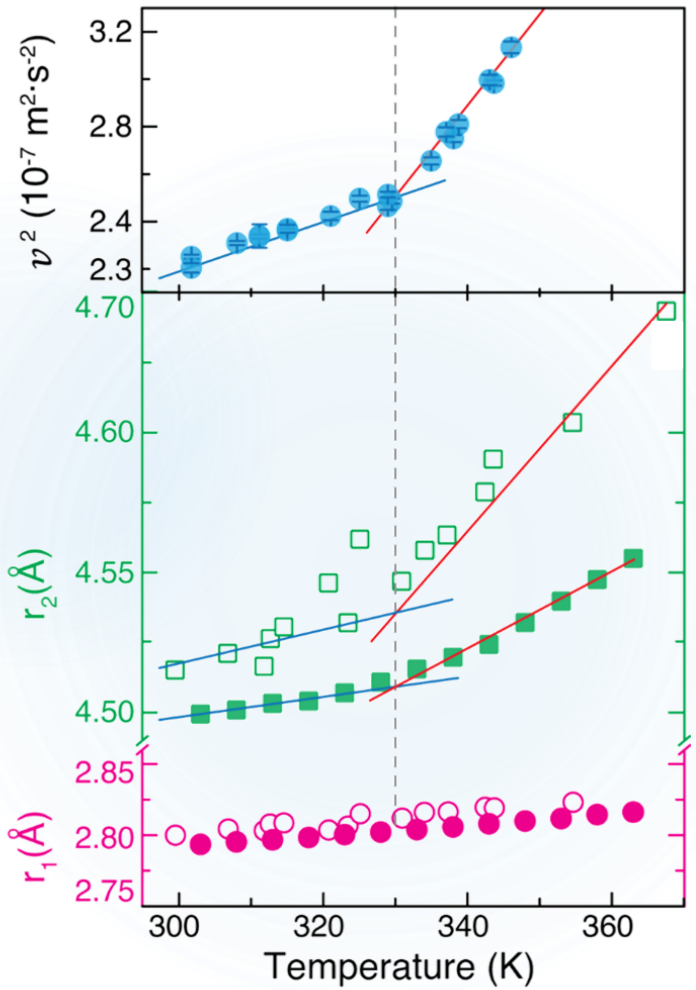
further tetrahedral order may arise when the fifth neighbor is considered

HIGH DENSITY





Rapid growth of hydrogen-bond network at ~330 K impacting r_1 and r_2



- Experimental results (square of the Brownian velocity)

- Experimental results (Skinner et al.)
- Numerical results (**THIS WORK**)

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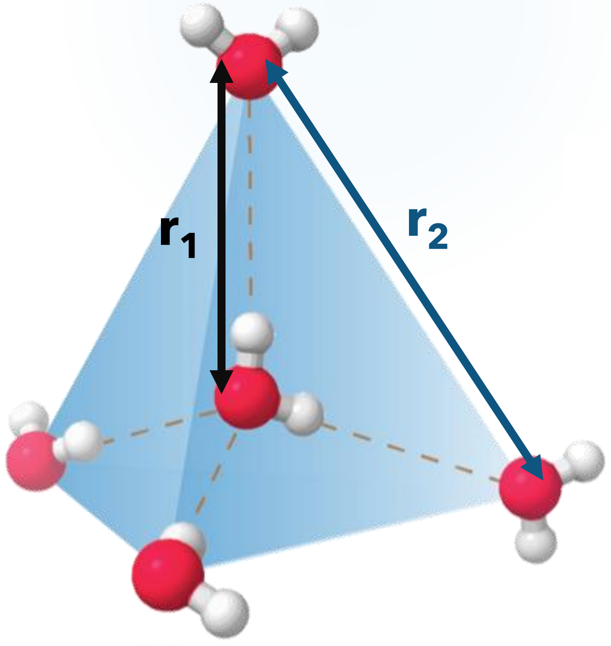
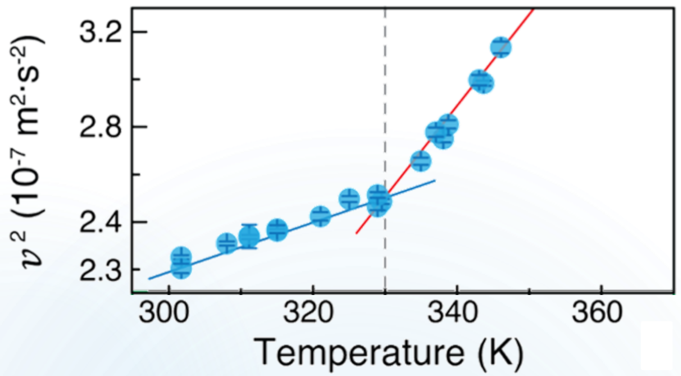
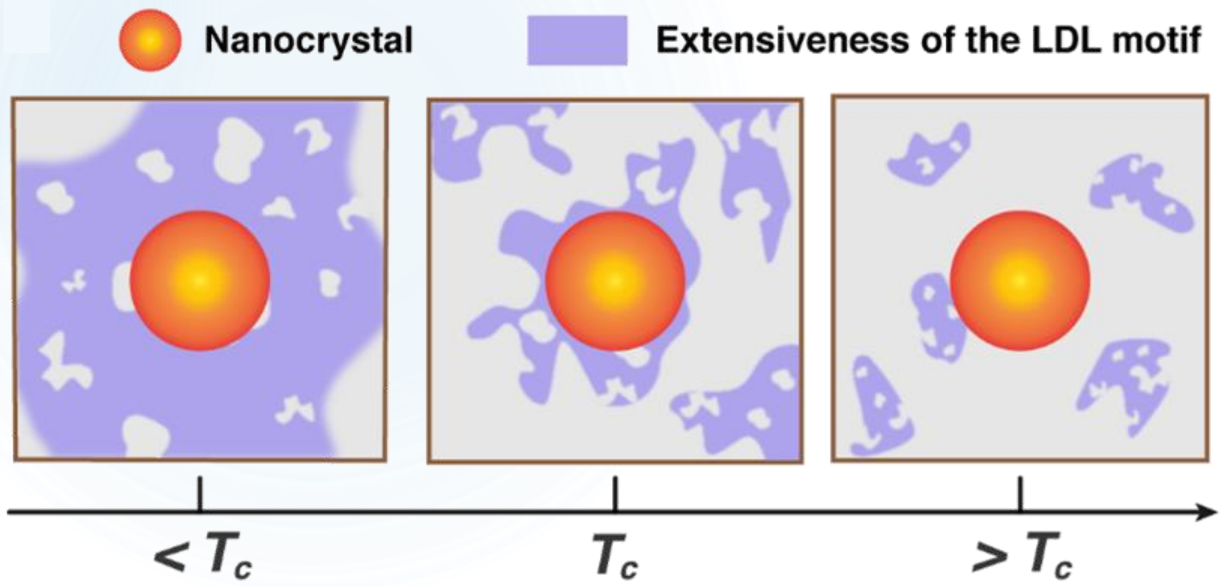
- Numerical results (**THIS WORK**)



Rapid growth of hydrogen-bond network at ~330 K



- Experimental results (square of the Brownian velocity)



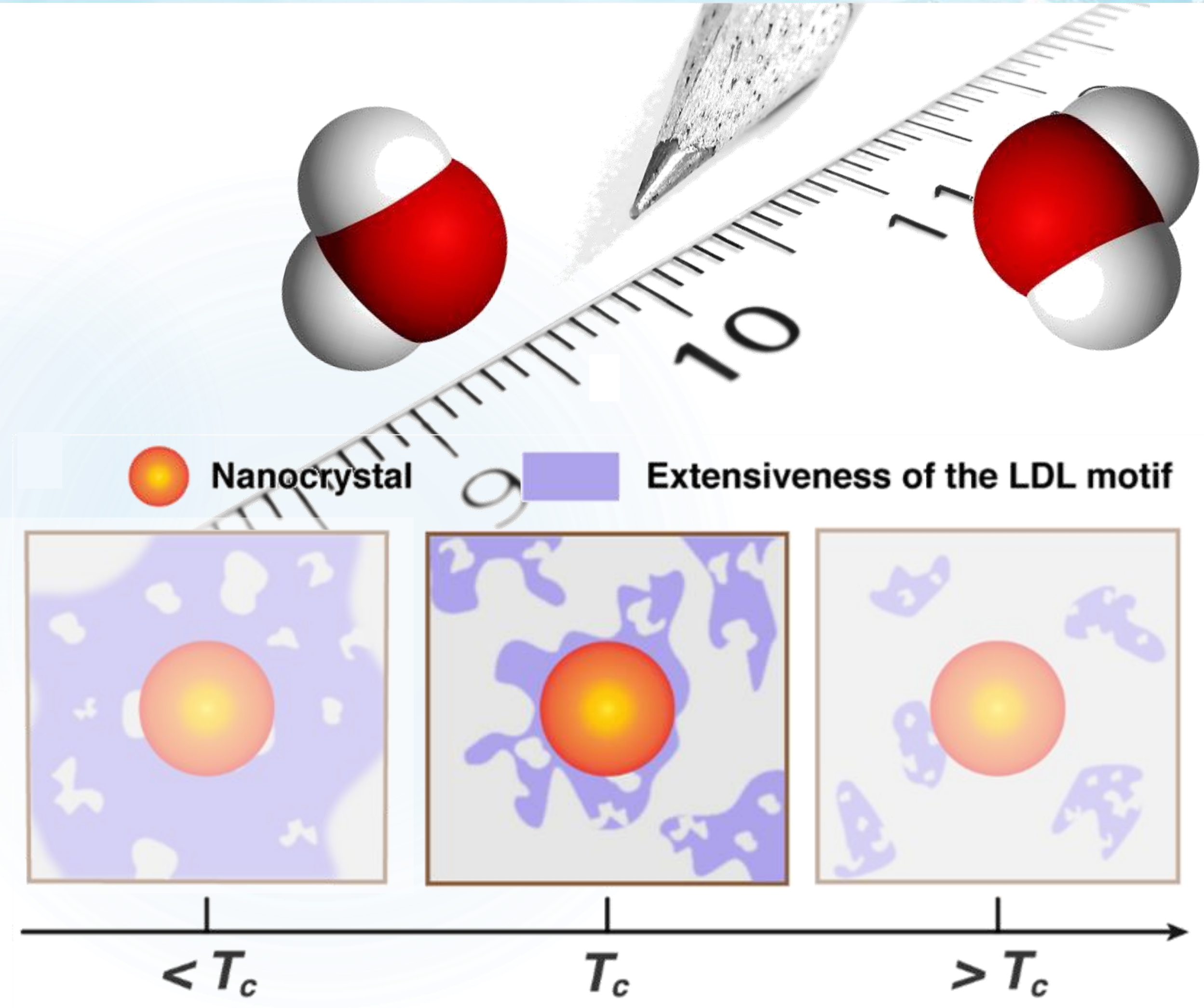
From the energy equipartition theorem results

$$\boxed{v_B^2 \propto \frac{T}{m^*}}$$

T – temperature
m*- effective mass (NP + displaced fluid)

- ✓ v_B increase with the T increase
- ✓ $v_B(T)$ slope increases for $T > T_c$ (lower effective mass)

The nanoparticle as a ruler for scanning the structural changes



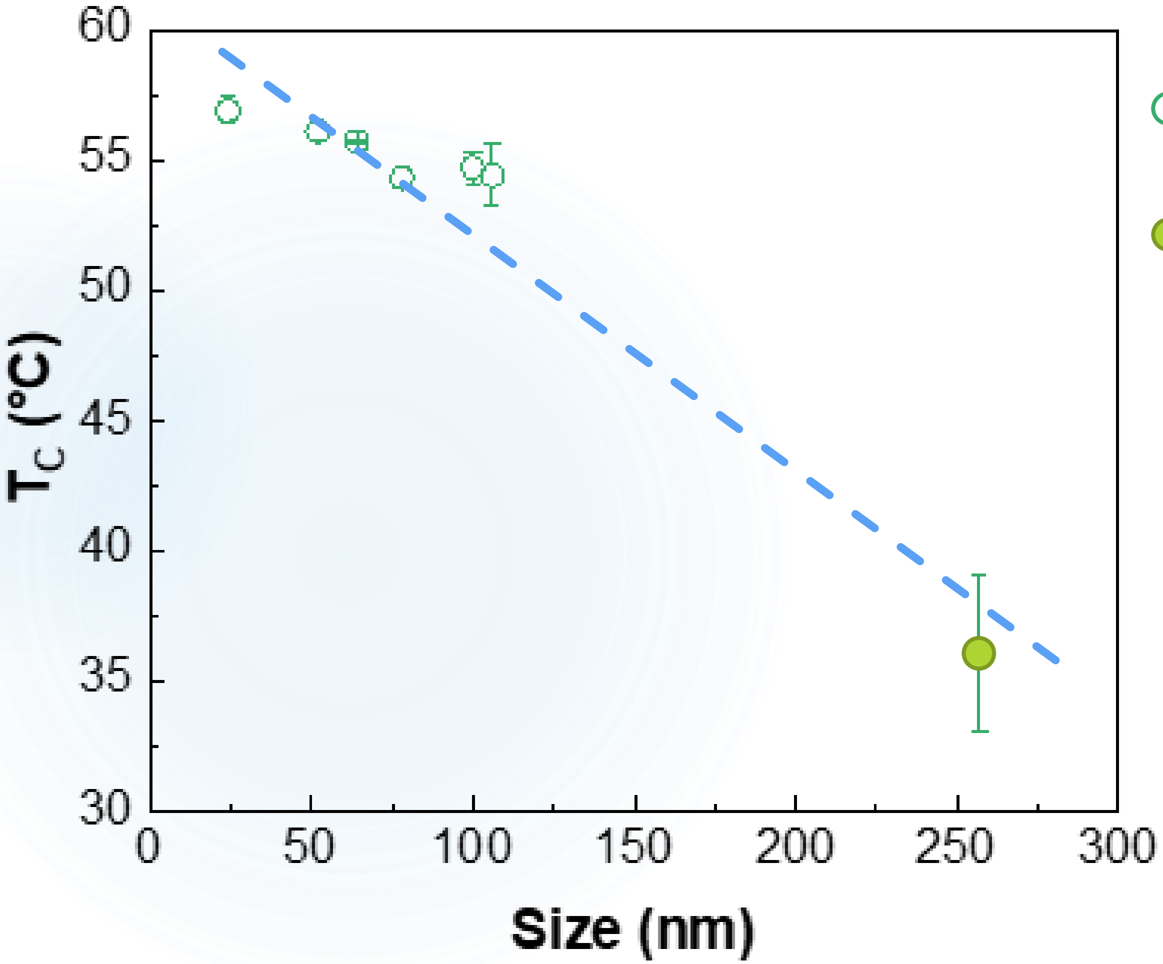
From the energy equipartition theorem results

$$\boxed{v_B^2 \propto \frac{T}{m^*}}$$

T – temperature
m*- effective mass (NP + displaced fluid)

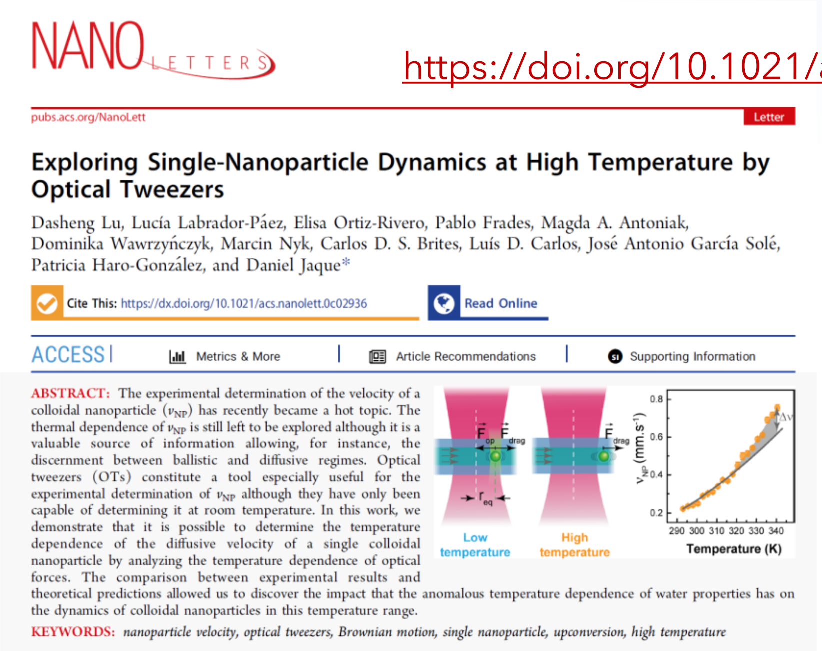
- v_B increase with the T increase
- $v_B(T)$ slope increases for $T > T_c$ (lower effective mass)
- **At T_c the NP size is similar to that of the LDL motif** (the NP is a ruler to measure the LDL extension)

Unpublished work



- Our results
- Optical tweezers

https://doi.org/10.1021/acs.nanolett.0c02936



NANO LETTERS

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Letter

Exploring Single-Nanoparticle Dynamics at High Temperature by Optical Tweezers

Dasheng Lu, Lucía Labrador-Páez, Elisa Ortiz-Rivero, Pablo Frades, Magda A. Antoniak, Dominika Wawrzyńczyk, Marcin Nyk, Carlos D. S. Brites, Luís D. Carlos, José Antonio García Solé, Patricia Haro-González, and Daniel Jaque*

Cite This: https://dx.doi.org/10.1021/acs.nanolett.0c02936

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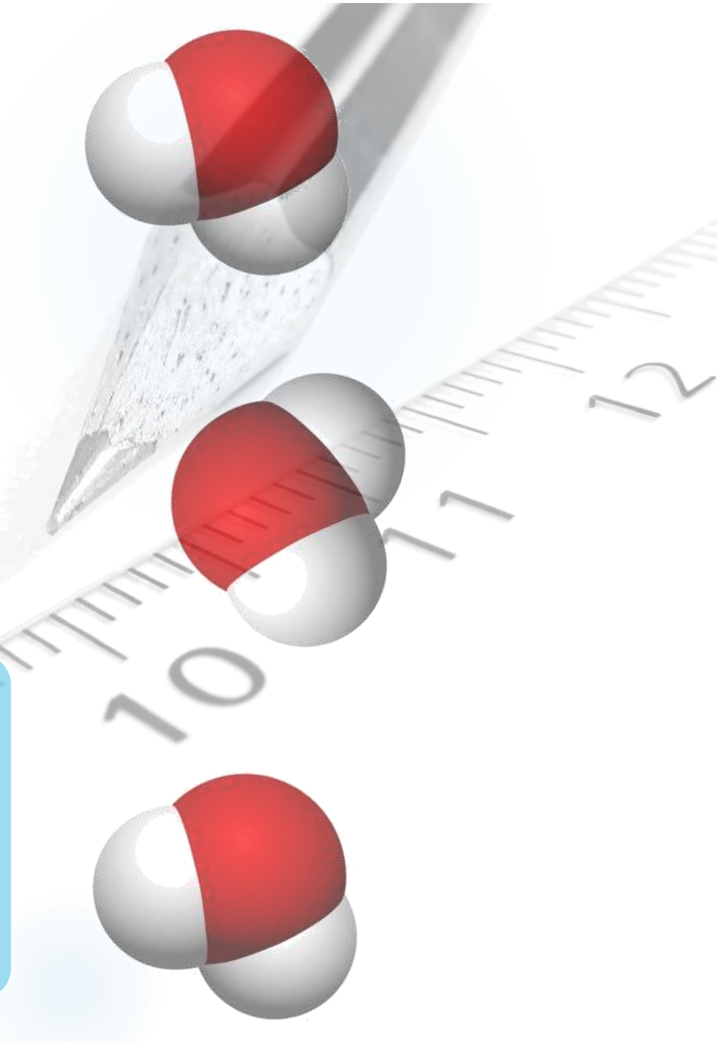
ABSTRACT: The experimental determination of the velocity of a colloidal nanoparticle (v_{NP}) has recently became a hot topic. The thermal dependence of v_{NP} is still left to be explored although it is a valuable source of information allowing, for instance, the discernment between ballistic and diffusive regimes. Optical tweezers (OTs) constitute a tool especially useful for the experimental determination of v_{NP} although they have only been capable of determining it at room temperature. In this work, we demonstrate that it is possible to determine the temperature dependence of the diffusive velocity of a single colloidal nanoparticle by analyzing the temperature dependence of optical forces. The comparison between experimental results and theoretical predictions allowed us to discover the impact that the anomalous temperature dependence of water properties has on the dynamics of colloidal nanoparticles in this temperature range.

KEYWORDS: *nanoparticle velocity, optical tweezers, Brownian motion, single nanoparticle, upconversion, high temperature*

Conclusions

- Using **suspended nanocrystals as rulers**, we have been able to **detect a crossover temperature** (T_c) in the nanoparticle's **instantaneous Brownian velocity in water**
- **At T_c the size of the nanoparticle and the LDL motif are comparable**.
- **This rapid change** of the size of the LDL motif at around 330 K is a **result of an underlying percolation transition**.



This technique can be **key to decipher the behaviour of water**, understanding the temperature dependence of its length scale will provide insight into the properties, as well as the mechanisms, functions, and roles of water (e.g. stability of proteins)

Acknowledgments

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- **Portuguese** This work was partially developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. (NANOHEATCONTROL - POCI-01-0145-FEDER-031469 funded by FEDER, through POCI and by national funds, OE, through FCT/MCTES).
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