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

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

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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 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

NaYF₄:Yb/Er(18/2%)@NaYF₄ core-shell NPs (24 nm)

Ligand-free NaYF₄:Lu/Yb/Er (50/18/2%) nanoparticles (106 nm)
EXPERIMENTAL
Structural Characterization

24 nm (pH=5.10)

106 nm (pH=5.20)
EXPERIMENTAL

Upconverting Thermometry

\[ T_0 = 302 \text{ K} \]

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

EXPERIMENTAL
Accessing the Brownian Velocity

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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)
The bilinear behavior is clearly discerned in water, depending on the pH and NP size near the water’s compressibility minimum.
The water’s tetrahedral arrangement describes the structure of the liquid water at lower temperatures.
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.
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Rationalizing the observed changes in the Brownian velocity through a percolating network of low- and high-density liquid water.
LIQUID WATER is a mixture of two hydrogen-bonding structures

\[
\text{liquid water} = \text{Less dense favored at low temperature} + \text{More dense favored at high temperature}
\]
Several recent references present a similar description for liquid water.
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.
Each molecule in water has different TETRAHEDRAL orientational order

\[ q = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \left( \cos \psi_{jk} + \frac{1}{3} \right)^2 \]
A percolation phase transition might explain our observations.

**tetrahedral state (TH)**
- maximal tetrahedral order among the nearest four neighbors

**disrupted state (DT)**
- further tetrahedral order may arise when the fifth neighbor is considered
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)

Experimental results (Skinner et al.)
Numerical results (THIS WORK)
Rapid growth of hydrogen-bond network at ~330 K

From the energy equipartition theorem results

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

\(T\) - 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

\[ \nu_B^2 \propto \frac{T}{m^*} \]

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

- \( \nu_B \) increase with the T increase
- \( \nu_B(T) \) 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)
Our results
Optical tweezers

Unpublished work

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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).
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