

# Decoding a Percolation Phase Transition of Water at $\sim 330$ K with a Nanoparticle Ruler

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

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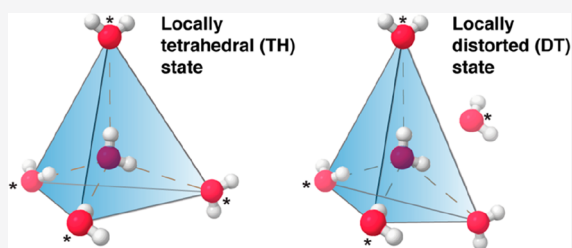
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**ABSTRACT:** Liquid water, despite its simple molecular structure, remains one of the most fascinating and complex substances. Most notably, many questions continue to exist regarding the phase transitions and anomalous properties of water, which are subtle to observe experimentally. Here, we report a sharp transition in water at 330 K unveiled through experimental measurements of the instantaneous Brownian velocity of NaYF<sub>4</sub>:Yb/Er upconversion nanoparticles in water. Our experimental investigations, corroborated by molecular dynamics simulations, elucidate a geometrical phase transition where a low-density liquid (LDL) clusters become percolated below 330 K. Around this critical temperature, we find the sizes of the LDL clusters to be similar to those of the nanoparticles, confirming the role of the upconversion nanoparticle as a powerful ruler for measuring the extensiveness of the LDL hydrogen-bond network and nanometer-scale spatial changes (20–100 nm) in liquids. Additionally, a new order parameter that unequivocally classifies water molecules into two local geometric states is introduced, providing a new tool for understanding and modeling water's many anomalous properties and phase transitions.



Water is the most important liquid for the existence of all life on Earth. Though it is the most common liquid, it is also the most uncommon in its behaviors, exhibiting a range of anomalous properties such as increased density upon melting, density maximum at 277 K (4 °C), reduced viscosity under pressure at below 306 K (33 °C), high surface tension, and decreased isothermal compressibility and heat capacity with temperature at ambient conditions (minimum values at 319 K (46 °C) and 308 K (35 °C), respectively).<sup>1–3</sup> In fact, it is quite questionable if life could have developed on the planet without these anomalous behaviors of water.<sup>4,5</sup> To explain these anomalous behaviors, the hypothesis of two organizations of hydrogen bonds competing at thermal equilibrium has been proposed.<sup>3,6–11</sup> These two hydrogen-bond organizations manifest as two phases, namely, the low-density liquid (LDL) and the high-density liquid (HDL), in the supercooled regime.<sup>12–15</sup> However, at ambient conditions, the existence of two distinct structural organizations and their implications remain elusive and controversial.

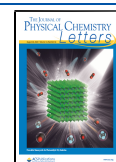
In the supercooled regime, the LDL is a predominantly low-energy hydrogen-bonded open tetrahedral configuration, while the HDL is a collection of interpenetrating shorter-ranged hydrogen-bond networks.<sup>3,16–19</sup> Despite the observation of the coexistence of these two structural motifs of water through spectroscopy<sup>20,21</sup> and scattering measurements,<sup>22–25</sup> the liquid structure inferred from these experiments is strongly debated. In this context, there is an intense demand for experimental techniques to microscopically decipher water's hydrogen-bonding structure.

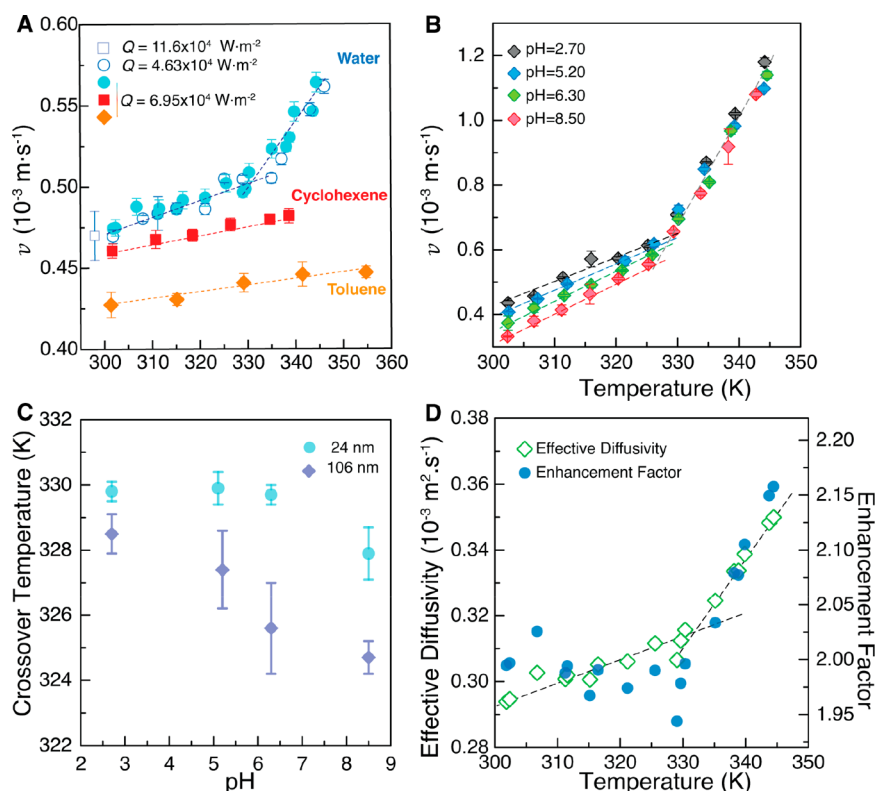
Recently, upconversion nanothermometry was utilized to measure the instantaneous Brownian velocity of luminescent nanocrystals suspended in liquids.<sup>26</sup> Because the instantaneous Brownian velocity is sensitive to the local liquid environment, we use this method to measure the LDL motif that is known as a large tetrahedral network featuring strong cooperativity.<sup>27</sup> As a proof-of-concept experiment, we prepared and measured the instantaneous Brownian velocity of luminescent nanofluids containing NaYF<sub>4</sub>:Yb/Er@NaYF<sub>4</sub> and NaYF<sub>4</sub>:Lu/Yb/Er upconversion nanocrystals of 24 and 106 nm in diameter, respectively, dispersed in water, cyclohexene, and toluene with volume fractions ( $\phi$ ) of 0.085% and 0.066%, for the smaller and bigger nanocrystals, respectively (Supplementary Figures S1 and S2 and Tables S1 and S2). The experimental setup is similar to that in ref 26 and is detailed in Supporting Information. Whereas for cyclohexene and toluene the Brownian velocities increase linearly with increasing temperature, for water a bilinear behavior with a crossover temperature  $T_c = 329.9 \pm 0.5$  K (57 °C) for the 24 nm nanoparticles (pH 5.10  $\pm$  0.01) and  $T_c = 327.4 \pm 1.2$  K (54 °C) for the 106 nm nanoparticles (pH 5.20  $\pm$  0.01) is clearly

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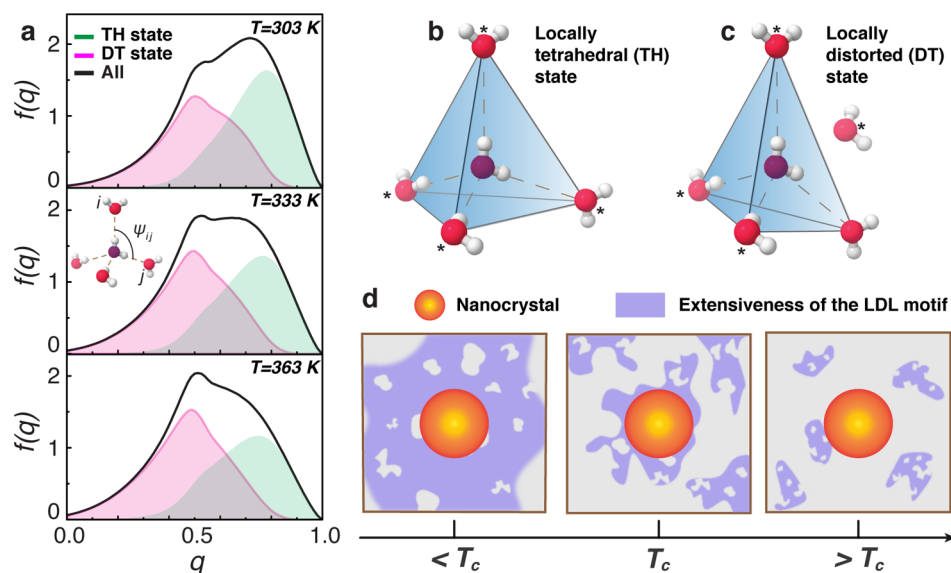
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**Figure 1.** Dependence of the instantaneous Brownian velocity of the upconverting nanocrystals on the initial temperature and pH of the suspensions. (a) Temperature-dependent instantaneous Brownian velocities of the 24 nm nanoparticles suspended in water ( $\text{pH } 5.10 \pm 0.01$ ), cyclohexene and toluene at initial (equilibrium) temperatures between 300 and 355 K. Vertical error bars represent mean  $\pm$  SD, whereas the uncertainty in the temperature values (thermocouple accuracy, 0.1 K) is too small to be discernible in the plots. The Brownian velocities are independent of the heat flux transferred to the nanofluid ( $Q$ ). The open square depicts data previously reported in similar upconverting nanoparticles.<sup>26</sup> The crossing of the two straight lines in the water suspensions corresponds to the crossover temperature  $T_c$ . (b) Temperature dependence of the Brownian velocity of the 106 nm nanoparticles in water suspensions with distinct pH values. (c) The dependence on pH of the crossover temperatures. (d) Effective diffusivity and enhancement factor of the nanofluid with 24 nm nanoparticles ( $\text{pH } 5.10 \pm 0.01$ ) with respect to pure water. All lines are the best fits to straight lines (slopes and correlation coefficients  $r^2$  are shown in Supplementary Table S3).



**Figure 2.** Structural investigations of liquid water. (a) Probability density function  $f(q)$  of the orientational order parameter  $q$  (eq 1) for water at 303, 333, and 363 K, calculated based on the molecular dynamics simulation of a cubic box of 1024 water molecules with the polarizable SWM4-NDP water model. The contributions toward  $f(q)$  of the locally tetrahedral (TH) state and the locally disturbed (DT) state are shown as shaded areas. (b and c) Schematics of the molecular arrangements around a water molecule (denoted with oxygen atoms in purple) in the TH state and the DT state. The asterisk next to the oxygen atoms denotes the four nearest neighbors. (d) Schematic of the length scale of the LDL motif (in purple) made up of connected TH-state molecules in comparison to the nanoparticle size (in orange).

discerned (Figure 1a,b and Supplementary Figures S9–S14). Moreover, for  $T > T_c$ , there is a noticeable increase in the slope of the linear correlation between  $\nu$  and  $T$  (Supplementary Table 3). These values of  $T_c$  are within the range of those reported for different physical properties of liquid water: thermal conductivity ( $337 \pm 5$  K), proton spin–lattice relaxation time ( $323 \pm 5$  K), refractive index ( $323 \pm 5$  K), conductivity ( $326 \pm 5$  K), surface tension ( $330 \pm 5$  K), and kinetic viscosity ( $323 \pm 6$  K),<sup>11</sup> as described in Supplementary Figure 12. Moreover, this bilinear trend was also observed in studies involving metallic nanoparticles,<sup>28</sup> colloidal  $\text{Ln}^{3+}$ -based nanocrystals,<sup>29</sup>  $\text{Eu}^{3+}$  aqueous complexes,<sup>30,31</sup> and organic molecules.<sup>32,33</sup>

The bilinear behavior observed in the instantaneous velocity of nanoparticles in water indicates two regimes of nanoparticle motion, where the nanoparticles exhibit a different effective mass  $m^*$ , signaling a change in the water–nanoparticle interaction. For a nanoparticle 24 nm in diameter,  $m^*$  changes drastically at  $T_c$  because the slope of  $\nu^2$  versus  $T$  for  $T > T_c$  increases 4- to 5-fold relative to that for  $T < T_c$  (Figure 2a and Supplementary Table S4), based on the equipartition theorem  $\nu^2 = k_B T / m^*$ . Because the effective mass is influenced by both the nanoparticle's mass  $m_N$  and the mass of the fluid  $m_C$  moving cooperatively with the nanocrystal, the drastic alteration of effective mass at  $T_c$  indicates a discontinuous change in the amount of fluid that moves cooperatively with the nanoparticle. By estimating the size of the LDL motif (Supporting Information Section 2.1), we find a plausible mechanistic explanation that, at  $T_c$ , the sizes of LDL motifs and nanoparticles are comparable, so that below  $T_c$  the nanocrystal has to move collectively with the surrounding LDL motif (Figure 2d). In this respect, by measuring the  $T_c$  one may use the nanoparticle as a ruler to measure the size of the LDL motif.

To rationalize the transition observed in the nanoparticles' effective mass, we investigate the underlying local order of the liquid water through molecular dynamics (MD) simulation based on the polarizable SWM4-NDP water model.<sup>34</sup> Because the tetrahedral geometry is key to distinguish the two different structures as the low-density water is thought to be more “ice-like”,<sup>35</sup> we first examine a tetrahedral orientational order parameter  $q$  for each water molecule,<sup>36,37</sup> given by

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

This  $q$ -value considers the relative angular positions in the four nearest neighbors around each water molecule. The summations run over all six  $jk$  pairs among the four nearest neighbors.  $\psi_{jk}$  denotes the angle extended from the oxygen atom of the molecule to the oxygen atoms of neighbors  $j$  and  $k$  (inset of Figure 2a). The  $q$ -value grows with the tetrahedral order around a molecule, with its average value equal to one for ordinary ice and zero for an ideal gas. At ambient conditions, the probability density function  $f(q)$  exhibits two overlapping peaks (Figure 2a): one at higher  $q$  that decreases with temperature and the other at lower  $q$  that increases with temperature.<sup>37</sup> These two peaks suggest the existence of two local structural states of water with different tetrahedral orders, but to date, their origin has not been elucidated.

Here, we introduce a new method to classify water molecules into two local structural states that give rise to the two peaks in  $f(q)$ . Because the peak at higher  $q$  indicates a state

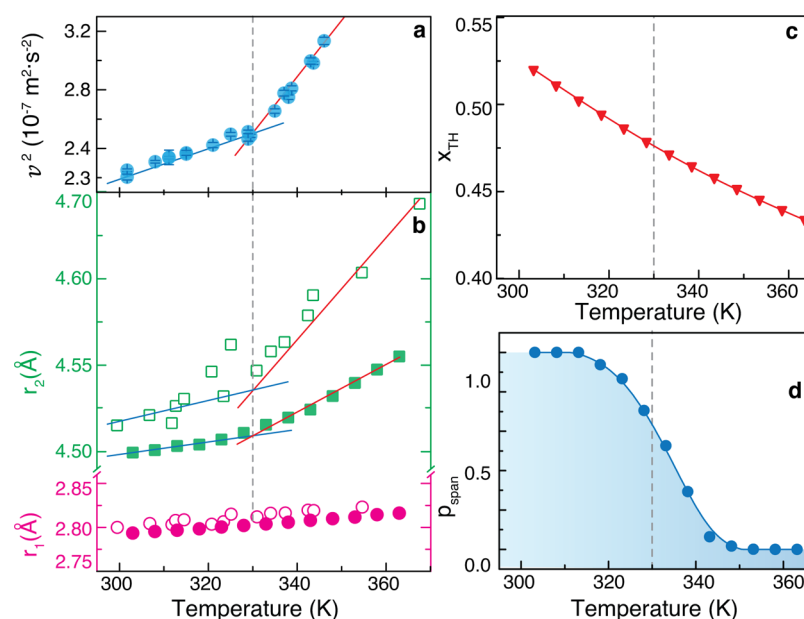
with a higher tetrahedral order, the positions of the four nearest neighbors are close to the vertices of a regular tetrahedron (Figure 2b). We denote this state as the locally tetrahedral (TH) state. The peak at lower  $q$ , on the other hand, indicates a state with less tetrahedral order. Owing to the open configuration in the TH-state, the second state involves an additional water molecule at an interstitial site that makes the liquid structure more tightly packed. We denote this state as the locally distorted (DT) state (Figure 2c). For a molecule in the DT-state, as the newly added molecule may become one of the four nearest neighbors, greater tetrahedral order may be found when the fifth nearest neighbor is taken into account. Therefore, we consider a generalized tetrahedral orientational order parameter  $q_5$  to be given by the maximum value of  $q$  for any 4 out of the 5 nearest neighbors (see the Supporting Information for a detailed description):

$$q_5 = \max_{\substack{\text{any 4 out of} \\ 5 \text{ nearest} \\ \text{neighbors}}} \left[ 1 - \frac{3}{8} \sum_{jk} \left( \cos \psi_{jk} + \frac{1}{3} \right)^2 \right] \quad (2)$$

where the summation runs over all pairs  $jk$  among the 4 chosen neighbors. A comparison between  $q$  and  $q_5$  allows us to distinguish the two local structural states. In the TH state, the 4 nearest neighbors give the maximal tetrahedral order, and thus  $q_5 = q$ . In contrast, in the DT state, the maximal tetrahedral order arises when the fifth nearest neighbor is considered, and thus  $q_5 > q$ . With this rule distinguishing the two underlying states, the two closely spaced peaks in  $f(q)$  (Figure 2a) are decoupled. In view of the simplicity of this classifying rule, the decoupling of the two states is considered effective, despite a slight shoulder peak that can still be discerned in the distribution of the DT state. Additional simulations based on the TIP4P-FB water model<sup>38</sup> support the two-state behavior observed in the SWM4-NDP model (see the Supporting Information). While there have been attempts to elucidate the two-state nature of water,<sup>7,11,39–41</sup> to the best of our knowledge, this is the first rule that allows one to classify water molecules into two states without introducing *ad hoc* cutoff values or fitting parameters.

Connected TH-state molecules can form a long-ranged hydrogen-bond network, consistent with the LDL liquid structure as a large tetrahedral network featuring strong cooperativity.<sup>27</sup> In contrast, such cooperativity is much weaker in the HDL motif formed by the DT-state molecules, in which the hydrogen bond network is less structured and shorter-ranged. Because of the two-state nature of the hydrogen-bond network, there is necessarily a geometric percolation transition that is not thermodynamic in origin. Although the two motifs interpenetrate with each other, the network formed by TH-state molecules is long-ranged and is consequential for transport properties on a larger length scale. It should be noted that the TH-state defined here is not equivalent to the low-density state that is defined elsewhere,<sup>7,42,43</sup> and the connection between different two-state classifications is a subject of future work.

With nanoparticles of different sizes, the difference between  $T_c$  values of smaller and bigger nanocrystals is, in all the pH range tested, around 3 K (Figure 1c), suggesting a drastic change in the length scale of the LDL motif around  $T_c$  (Supplementary Figure S11). This suggests that the fluctuations of LDL motifs become correlated and grow in spatial



**Figure 3.** Brownian velocity of the upconverting nanocrystals versus liquid water structural data. (a) Temperature dependence of the square of the instantaneous Brownian velocity of the 24 nm nanocrystals in water suspension. The straight lines are the best fit to the experimental data ( $r^2 > 0.989$  and correlation coefficients in Supplementary Table S7). (b) Simulated and experimental data on the positions of the first maximum ( $r_1$ ) and second maximum ( $r_2$ ) in the O–O pair distribution function. The open circles and squares depict high-energy X-ray diffraction data and the solid circles and squares result from the MD simulations of the SWM4-NDP water model, adapted (without error bars) from ref 23 (points below 300 K are not displayed). Copyright 2014. AIP Publishing. The straight lines are the best fit to the diffraction and simulation data (correlation coefficients in Supplementary Table S6). (c) Fraction of molecules in the TH-state,  $x_{\text{TH}}$ , computed from MD simulations of SWM4-NDP water model. (d) Estimated probability for finding an LDL motif spanning the size of a 24 nm nanocrystal, where a strong crossover from 1 to 0 is observed at around 330 K. The dashed lines indicate the crossover temperature observed in the instantaneous Brownian velocity of 24 nm nanocrystals.

extent below  $T_c$ ,<sup>3,44</sup> and this could be due to the underlying percolation transition such that the LDL motif formed by TH-state molecules becomes percolated below  $T_c$ . While liquid water has been known to be a large cluster of connected hydrogen-bonded network,<sup>45–47</sup> here, we are concerned with the more tetrahedrally structured network formed by TH-state molecules. Although individual hydrogen bonds in the network have short lifetime, they are likely to reform because of the favorable tetrahedral geometry. Therefore, the network formed by TH-state molecules would be more cooperative over a longer range and more persistent. Moreover, it should be noted that the LDL motifs cannot be thought of as density heterogeneities measured by small-angle X-ray scattering (SAXS) measurements (dimensions of the order of 1 nm at ambient conditions).<sup>16,48,49</sup> The LDL motifs are formed by a tetrahedral (ice-like) network of TH-state molecules with many empty pockets between the less-ordered, shorter-ranged HDL water network (dominant in ambient conditions) and thus are larger than the density heterogeneities measured by SAXS measurements (regions occupied by TH-state molecules exclusively). Upon computing the fraction of TH-state molecules (Figure 3c),  $x_{\text{TH}}$ , we notice that the fraction at  $T_c \approx 330$  K is close to the site percolation threshold for a diamond lattice,  $x_{c,\text{diamond}} \approx 0.43$ .<sup>50</sup> On the basis of molecular configurations sampled in MD simulations, we estimate the probability of finding an LDL motif spanning the size of the 24 nm nanoparticle and observe that this probability changes rapidly from 1 to 0 around  $T_c$  (Figure 3d, calculation details in the Supporting Information), consistent with the behavior of a percolation transition.<sup>50</sup>

Because of this transition, there is a swift crossover in many water properties. Below  $T_c$ , LDL motifs span the liquid,

increasing the structural fluctuation between the two classes of H-bond networks. Above  $T_c$ , LDL structures are short-ranged such that water behaves like a simple liquid. An example of the swift crossover has been observed in the position of the second maximum of O–O pair distribution function as a function of temperature obtained through high-energy X-ray-scattering measurements<sup>23</sup> and our MD simulations. While the position of the first maximum ( $r_1$ ) increases linearly with temperature, the second maximum ( $r_2$ ) exhibits a bilinear behavior with a crossover at  $T_c$  at around 330 K (Figure 3b). The agreement between X-ray diffraction and the simulation is remarkably close given that no simulation model exactly reproduces real water. The agreement between the  $T_c$  values of our experiment and of the  $v^2(T)$  and  $r_2(T)$  is also remarkable.

In a further set of experiments, we measured the temperature dependence of the Brownian velocity of colloidal nanocrystals in the water at pH values in the range of 2.70–8.50, as illustrated in Figure 1b. Notably, for both  $\text{NaYF}_4:\text{Yb}/\text{Er}$  and  $\text{NaYF}_4:\text{Lu}/\text{Yb}/\text{Er}$  nanocrystals, whereas for  $T > T_c$  the rate of increase of the Brownian velocity with temperature is independent of the nanofluid's pH, for  $T < T_c$  that rate changes with the pH in such a way that the Brownian velocity increases with decreasing pH (Figure 1b). Furthermore,  $T_c$  increases with decreasing pH (Figure 1c), suggesting  $\text{H}_3\text{O}^+$  increases the size of the LDL motif because its oxygen atom is  $\text{sp}^3$ -hybridized and, thus, geometrically similar to TH-state water molecules. However, the observed increase of the Brownian velocity with decreasing pH for  $T < T_c$  suggests that  $\text{H}_3\text{O}^+$  destabilizes the hydrogen-bond network in the LDL motif, making the network motion less cooperative.

Using a two-plate thermal diffusion model, we can accurately describe our measured instantaneous Brownian velocity with



thermal diffusion (see [Supporting Information](#)). The two-plate model predicts a linear trend of  $t_0$  versus  $x_i$  in [Figure S3](#) and shows a linear relationship between thermal diffusivity and the predicted velocity ([Supplementary Figures S15–S18](#)). Extrapolating this relation using the thermal diffusivity for pure water,<sup>51–53</sup> we predict the thermal diffusivity for the 24 nm nanoparticles suspended in water to be enhanced more than two times, as compared to that of pure water in the same temperature range ([Figure 1d](#)). Though this large enhancement is a prediction based on thermal modeling, it is within the range of enhancements observed experimentally in some nanofluids.<sup>54,55</sup> It is worth noting that our numerical model highlights the fact that the temperature detected by luminescence nanocrystals obeys macroscopic thermal transport. However, to understand the exact nature of the Brownian motion at nonequilibrium conditions, comprehensive models accounting for nanoconvection and other nanoscale effects are required. Additionally, effects of ions and the surface water structure on nanoparticles may be considered in a more comprehensive model of the system.

Using suspended nanocrystals as rulers, we have been able to detect a crossover temperature in the nanoparticle's instantaneous Brownian velocity in water, at which temperature 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. Because the long-range hydrogen-bond network in LDL motif is the key to decipher the behavior of water,<sup>56</sup> understanding the temperature dependence of its length scale will provide insight into the properties as well as the mechanisms, functions, and roles of water, for instance, in influencing the stability of proteins<sup>57,58</sup> and how they are denatured at temperatures close to the  $T_c$  value reported. Beyond the properties of water, the experimental technique of upconversion thermometry of suspended Brownian nanocrystals also has broader significance for probing interactions in fluids, for example, in the physics of the glass transition, where the cooperatively rearranging region in the glassy liquid is the central concept.<sup>59</sup>

## METHODS

**General Description.** We prepared luminescent nanofluids containing  $\text{NaYF}_4\text{:Yb/Er@NaYF}_4$  and  $\text{NaYF}_4\text{:Lu/Yb/Er}$  up-conversion nanocrystals of different sizes (24 and 106 nm in diameter, respectively) dispersed in water, cyclohexene, and toluene with volume fractions ( $\phi$ ) of 0.085% and 0.066%, for the smaller and bigger nanocrystals, respectively ([Supplementary Figures S1 and S2 and Tables S1 and S2](#)). For distinct initial equilibrium temperatures (ranging between 300 and 355 K), we heated the nanofluids and recorded their time-dependent emission spectra upon 980 nm excitation in different fixed positions along the  $xx$  direction ( $x_i = 0.2\text{--}0.9$  cm,  $i = 1\text{--}6$ , [Supplementary Figures S3 and S4](#)). For each time instance, the absolute temperature ( $T$ ) is calculated through the intensity ratio (the thermometric parameter  $\Delta$ ) between the  ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$  ( $I_H$ , 510–535 nm) and  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  ( $I_S$ , 535–565 nm)  $\text{Er}^{3+}$  emission bands, as<sup>26</sup>

$$\frac{1}{T} = \frac{1}{T_0} - \frac{k_B}{\Delta E} \ln \left( \frac{\Delta}{\Delta_0} \right) \quad (3)$$

where  $\Delta_0$  is the thermometric parameter at a reference temperature  $T_0$ ,  $k_B$  the Boltzmann constant, and  $\Delta E$  the energy gap between the  ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$  levels. The  $\Delta E$  and  $\Delta_0$  values

are determined independently by taking into account the barycenter of the  ${}^2\text{H}_{11/2}$  ( $\sim 525$  nm),  ${}^4\text{S}_{3/2}$  ( $\sim 545$  nm), and  ${}^4\text{I}_{15/2}$  energy levels and from the dependence with the laser excitation power of the thermometric parameter, respectively ([Supplementary Figures S5 and S6](#)). The thermometric parameter  $\Delta = I_H/I_S$  increases with rising temperature,<sup>26</sup> because the relative population of the  ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$  levels are in thermal equilibrium, following the Boltzmann's distribution.<sup>26</sup> In [Supplementary Figures S3a,b and S4](#) (where  $T$  is expressed as a reduced temperature, [Supporting Information](#)), a critical time  $t_{0i}$  is determined from the onset of change in the  $\text{Er}^{3+}$  upconversion induced by the temperature variation, and the slope of the line plot between  $x_i$  and  $t_{0i}$  gives the instantaneous Brownian velocity  $v$  of the suspended upconverting nanocrystals<sup>26</sup> ([Supplementary Figure 3c,d](#)). The critical time  $t_{0i}$  is determined from the onset of the temperature variation ([Supplementary Figures 3 and 4](#)) and the slope of the line plot between  $x_i$  and  $t_{0i}$  gives the instantaneous Brownian velocity  $v$  of the suspended  $\text{NaYF}_4\text{:Yb/Er@NaYF}_4$  and  $\text{NaYF}_4\text{:Lu/Yb/Er}$  upconversion nanocrystals (see ref 26 for details). For each fixed position  $x_i$ , we observe a marked decrease of  $t_{0i}$  with rising initial equilibrium temperature of the nanofluid ([Supplementary Figure 3c,d](#) for the illustrative example  $x_i = 0.8 \times 10^{-2}$  m).

**Preparation of Upconversion Nanocrystals.**  $\text{NaYF}_4\text{:Yb/Er}$  (18/2%)@ $\text{NaYF}_4$  (average diameter 24 nm) and  $\text{NaYF}_4\text{:Lu/Yb/Er}$  (50/18/2%) (average diameter 106 nm) nanocrystals were synthesized by a standard coprecipitation or modified hydrothermal method according to ref 60. Further experimental details are available in the [Supporting Information](#).

**Operating Procedure for Temperature Mapping.** In a typical experiment, a Thorlabs quartz cuvette (CV10Q1400) was used as the container and filled with 0.50 mL of nanofluid at an initial temperature between 300 and 355 K. For water suspensions, the pH ranges from 2.70 to 8.50 ( $\pm 0.01$ ). The nanofluid's temperature is further increased through the Joule effect using a Kapton thermofoil heater (Minco) in thermal contact with one side of the cuvette. The initial temperature of the nanofluids was measured by an immersed thermocouple (1620-20147, VWR) with an accuracy of 0.1 K, according to the manufacturer. Temperature increments of 10 and 15 K were generated corresponding to a heat flux transferred to the nanofluid ( $Q$ ) of  $4.64 \times 10^4$  and  $6.96 \times 10^4$   $\text{W}\cdot\text{m}^{-2}$ , respectively. A continuous-wave (CW) laser diode (980 nm, 0.5 W), positioned next to the container, is focused through an optical lens (7.5 cm focal distance) and is controlled by a moving stage with a minimum step of 0.001 mm. Under 980 nm excitation, the nanocrystals' upconversion emission is collected by a collimating lens (74-UV, Ocean Optics), and the signals are subsequently guided to the detector (Maya 2000 Pro, Ocean Optics) through a QP450-1-XSR optical fiber (Ocean Optics). The signals were denoised through the DWT procedure. Further experimental details and experimental data treatments are available in the [Supporting Information](#).

**Molecular Dynamics Simulation of Water.** Molecular dynamics simulation for the polarizable SWM4-NDP water model<sup>34</sup> was carried out using an extended Lagrangian dynamics with a dual-Langevin thermostat<sup>61</sup> with the OpenMM package.<sup>62</sup> At each temperature, the size of the cubic simulation box was set such that the density of water molecules in the simulation box matched the density of water at atmospheric pressure ([Supplementary Table S6](#)). Periodic boundary conditions are applied. For the dual-Langevin thermostat, the friction

coefficients for the center-of-mass and for the internal Drude-pair degrees of freedom were  $20 \text{ ps}^{-1}$  and  $1 \text{ ps}^{-1}$ , respectively, and the temperature set for the internal Drude-pair was 1 K. The time step for the integration was 1 fs. For each randomly generated initial configuration, the system was first annealed from 373.15 K to the desired temperature in 100 equal-interval temperature steps and 1 ps per step, followed by equilibration at the desired temperature for 1 ns. Then, the configuration state of the water was sampled every 10 ps for 70 ns. The sampling was repeated independently for 8 times for each system size and temperature.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02147>.

Nanoparticle synthesis, materials characterizations, computational methods, study of the effective mass of the nanoparticles, and investigation of instantaneous Brownian velocity and thermal diffusivity (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Bilin Zhuang** – Institute of High Performance Computing, Singapore 138632 Singapore; Yale-NUS College, Singapore 138527 Singapore; Email: [zhuangbl@ihpc.a-star.edu.sg](mailto:zhuangbl@ihpc.a-star.edu.sg)

**Xiaogang Liu** – Department of Chemistry, National University of Singapore, Singapore 117543 Singapore; Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Fuzhou 350207, P.R. China; [orcid.org/0000-0003-2517-5790](https://orcid.org/0000-0003-2517-5790); Email: [chmlx@nus.edu.sg](mailto:chmlx@nus.edu.sg)

**Luís D. Carlos** – Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, Universidade de Aveiro, 3810–193 Aveiro, Portugal; [orcid.org/0000-0003-4747-6535](https://orcid.org/0000-0003-4747-6535); Email: [lcarlos@ua.pt](mailto:lcarlos@ua.pt)

### Authors

**Carlos D. S. Brites** – Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, Universidade de Aveiro, 3810–193 Aveiro, Portugal; [orcid.org/0000-0001-9636-2628](https://orcid.org/0000-0001-9636-2628)

**Mengistie L. Debasu** – Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics and Department of Chemistry and CICECO – Aveiro Institute of Materials, Universidade de Aveiro, 3810–193 Aveiro, Portugal; [orcid.org/0000-0003-2516-9665](https://orcid.org/0000-0003-2516-9665)

**Ding Ding** – Institute of Materials Research and Engineering, Singapore 138634 Singapore

**Xian Qin** – Department of Chemistry, National University of Singapore, Singapore 117543 Singapore

**Fernando E. Maturi** – Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, Universidade de Aveiro, 3810–193 Aveiro, Portugal

**Winnie W. Y. Lim** – Institute of High Performance Computing, Singapore 138632 Singapore

**De Wen Soh** – Institute of High Performance Computing, Singapore 138632 Singapore

**J. Rocha** – Department of Chemistry and CICECO – Aveiro Institute of Materials, Universidade de Aveiro, 3810–193 Aveiro, Portugal; [orcid.org/0000-0002-0417-9402](https://orcid.org/0000-0002-0417-9402)

**Zhigao Yi** – Department of Chemistry, National University of Singapore, Singapore 117543 Singapore; [orcid.org/0000-0003-0853-2055](https://orcid.org/0000-0003-0853-2055)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02147>

## Author Contributions

<sup>†</sup>C.D.S.B. and B.Z. contributed equally to this work. C.D.S.B., B.Z., and L.D.C. conceived the project. B.Z., D.D., W.W.Y.L., and D.W.S. performed the simulations and theoretical calculations, whereas C.D.S.B., M.L.D., F.E.M., and Z.Y. performed the experiments. X.Q., J.R., B.Z., X.L., and L.D.C. provided input into the design of the experiments (the two last authors supervised the whole project). B.Z., D.D., X.L., and L.D.C. cowrote the manuscript with input from other authors.

## Notes

The authors declare no competing financial interest.

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