

## Our Nature Communications paper is out – ice-like optical phonons in liquid water

Posted on [January 15, 2016](#) by [Dan Elton](#)

Commentary by [Dan Elton](#)

Our paper, "[The hydrogen-bond network of water supports propagating optical phonon-like modes](#)" was published on January 4th in *Nature Communications* ([full pdf](#), [Stony Brook University Press Release](#)).

Our work shows that propagating vibrations or phonons can exist in water, just as in ice. The work analyzes both experimental data and the results of extensive molecular dynamics simulations performed with a rigid model (TIP4P/eps), a flexible model (TIP4P/2005f), and an *ab-initio* based polarizable model (TTM3F).

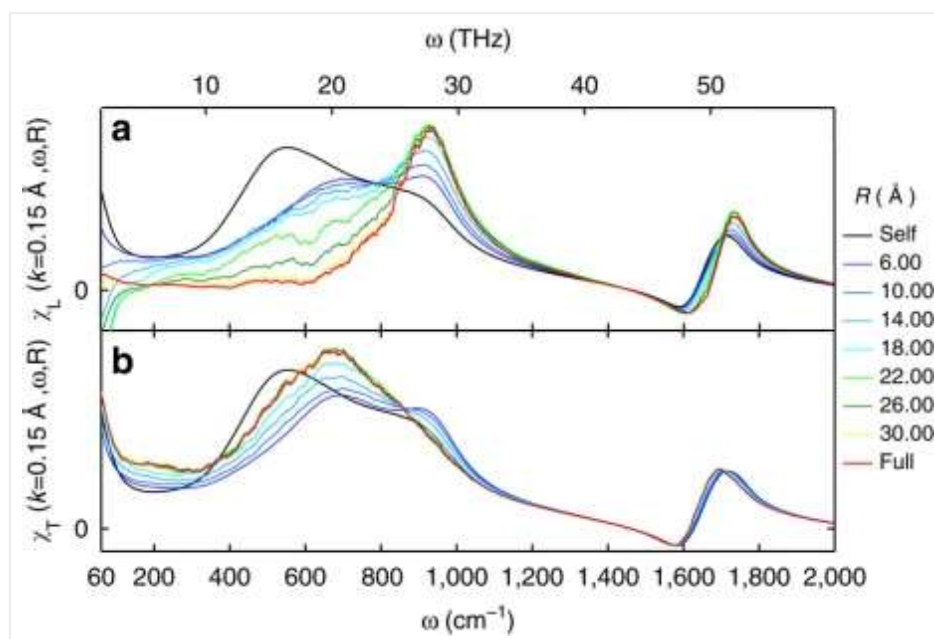
Many of these simulations were performed on the new supercomputing cluster at Stony Brook's [Institute for Advanced Computational Science](#).

### Liquid-state phonons

Phonons are usually considered to be solely a solid-state phenomena. In liquids, atoms or molecules are disordered and diffuse around, and there is no underlying order or crystal structure, so naively liquids should not be able to support coherent phonons. Water is special, however, because it contains a hydrogen bond network. We argue phonons can propagate through this H-bond network, just as they propagate through the H-bond network of ice.

Unlike in ice, however, hydrogen bonds in water are constantly being broken and reformed, so the phonons only last for at most one trillionth of a second (1 ps). However, over this short time we show they can travel over surprisingly long distances of 2+ nanometers.

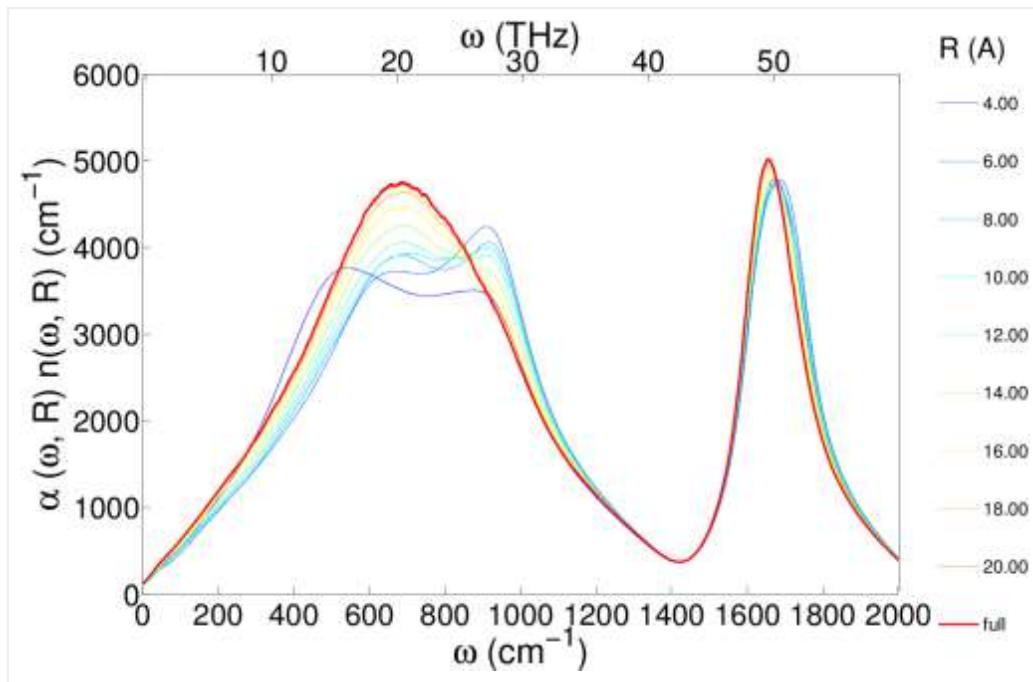
We verified this range by breaking the transverse and longitudinal dielectric spectra into distance-dependent components:



- Distance dependence of the longitudinal (top) and transverse (bottom) dielectric susceptibilities.

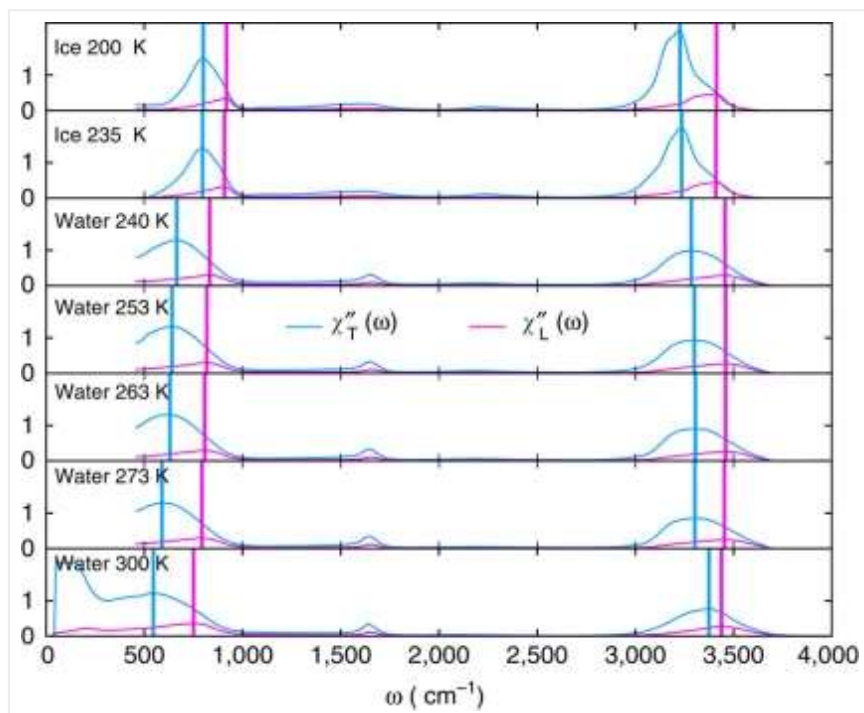
To make this plot we considered spheres of various sizes around each molecule and analyzed the spectra using those spheres. When the radius of the sphere,  $R$ , is zero, then you are only considering single molecules separately and not considering how the dipole moments of different molecules add together. When you start increasing  $R$ , then you start considering molecules within a sphere around each molecule. Molecules that have dipole moments pointing in the same direction are said to be positively correlated and such correlation increases the dielectric response. Molecules that point in opposite directions are anti-correlated and decrease the response. At some far enough distance, the molecules become uncorrelated. When  $R$  is larger than that distance, the spectra no longer changes. The largest  $R$  accessible in our 4 nm box would be along the diagonal, which is  $R = 3.46$ . Surprisingly, in the librational band, the spectra does not stop changing until  $R$  is greater than 2-3 nanometers. To put that in perspective, a 2 nanometer sphere contains over 1100 molecules! The picture we arrive at is that of an extended quasi-tetrahedral (ice-like) hydrogen bond network that exists on picosecond timescales and allows for phonons to propagate through it.

I also did a distance decomposed infrared spectra (unpublished), which shows the essentially the same information as the transverse dielectric susceptibility:



- Distance decomposed Infrared spectrum from a simulation of TIP4P/2005f water in a 4nm box.

We focused specifically on optical phonons, which correspond to charge density waves that can interact with electromagnetic waves. In the case of ice, optical phonons cause well documented peaks in infrared and polarized Raman spectra. Similar absorption peaks are also found in the infrared and depolarized Raman spectra of liquid water.



- Longitudinal (magenta) and transverse (cyan) dielectric susceptibilities of ice and water derived from experimental data. The lines are positioned at

the peak maxima and indicate LO-TO splitting.

By comparing the experimental Raman, dielectric, and infrared spectra we show that peaks the librational and OH-stretch parts of the Raman & infrared spectra correspond to two different types of phonons, longitudinal and transverse. We identify longitudinal modes by looking at the longitudinal dielectric susceptibility.

The shifting of the position of the longitudinal and transverse peaks with temperature can be related to important structural changes in the hydrogen bond network, providing a new window into how water's structure changes with temperature.

### **Relation to previous work**

Our work builds on previous work on the nonlocal ( $k$ -dependent) susceptibility of water. More importantly, though, our findings challenge older ideas about water's dynamics that characterized spectral peaks being due to the vibrational motions of at most a few molecules. In particular we reject previous interpretations of the librational band in Raman and IR spectra that assigned peaks to the librational motions of single molecules. Similarly, attempts to split the OH-stretching band cleanly into peaks from 2-Hbonded, 3-Hbonded, and 4H-bonded molecules are also called into question.

There is obviously some merit in understanding the spectra of bulk water by first studying the spectra of clusters of increasing size ([Saykally, 2001](#)). Under this approach it is usually implicitly assumed that when large clusters start to mimic the response of bulk water the size of such clusters indicates the spatial extent of vibrational excitations in the bulk. This is a questionable assumption. In some cases, particular clusters have been singled out as being particularly relevant to bulk water dynamics, in particular the cyclic pentamer ([Bosma 1993](#)). Our work contradicts the view that dynamics are confined to small clusters such as pentamers.

While unfortunately we did not get to reference it in our paper, [a recent work by Guardia, Skarmoutsos, and Masia](#) nicely compliments our findings. They performed a 15 ps CPMD simulation with the BLYP functional, and observe that the molecular dipole correlation functions vary depending on the initial h-bonding state of the molecules. Not surprisingly, molecules with fewer hbonds have faster dipole relaxation. Interestingly, they take the further step of analyzing the spectral density of molecules that start off initially with a different numbers of H-bonds. They find that the librational band maxima and shape changes dramatically depending on initial H-bond number. The bending peak does not change, while the OH-stretching band maxima is seen to shift. The OH-stretching peak shifts from 3406 for molecules with 0 H-bonds to 3250  $1/\text{cm}$  for molecules with 5 H-bonds. This redshifting of about 160  $1/\text{cm}$  is not unexpected. The librational band also exhibits a shift by about 200  $1/\text{cm}$ , but it is a *blueshift* in the opposite direction. This suggests that librational modes are sensitive to the degree of H-bonding. They also find that the librational band for molecules with 0 H-bonds is multimodal, exhibiting two clear peaks which likely correspond to the wagging and rocking librations we discuss in our paper.

### **Relevance to the water structure debate**

Discussion and debate about the structure of water goes back as far as 1892, when W.K. Roentgen proposed that water contains a mixture of two structural motifs – “ice like” and “liquid

like". Today, two state mixture models are still discussed, but with a more nuanced conception of the two states – typically described as LDL (low density liquid) and HDL (high density liquid).

The mixture model (the co-existence of two metastable liquid phases in fluctuating domains) is attractive for several reasons. Amorphous ice can be made in both LDA and HDA forms, and sharp phase transitions have been observed between the two forms ([video](#)). Clearly, the mixture model creates a framework by which one can make sense of the low temperature anomalies of water. This is true regardless of whether one subscribes to the liquid-liquid critical point hypothesis or the singularity-free view of water's phase diagram in the deeply-supercooled 'no-mans land'.

The present debate about the structure of water in large part originates from the publication of "[The inhomogeneous structure of water at ambient conditions](#)" by Huang, Nilsson, et al. in 2009. Their argument largely (but not entirely) rests on their interpretation of small angle X-ray scattering (SAXS) below  $.4 \text{ 1/\AA}$ , where a minima is observed at small  $q$  and enhancement is observed as  $q \rightarrow 0$ . The paper failed to find the enhancement when using the SPC/E model and therefore implied that MD simulation could not be trusted to correctly reproduce the structure of water. However, the region of small  $q$  is tricky to calculate from MD simulation, especially when Fourier transforming the structure factor as they did. Later MD simulation by [Sedlmeier, Horinek, and Netz](#) that used a better calculation method and larger box did recover a slight enhancement with SPC/E, and a more pronounced enhancement is observed with the more accurate TIP5P and TIP4P/2005 models.

### **How should the enhancement in $S(q)$ at small $q$ be interpreted?**

While molecular dynamics simulations of well-validated force-field models (ie. not ST2) do show co-existence of clearly defined HDL-like and LDL-like domains at very low temperature ([ref1](#), [ref2](#), [ref3](#)), simulations do not show such dramatic heterogeneity in room temperature water. The distributions of various local structure parameters ( $Q_4$ ,  $Q_6$ ,  $Sk$ ,  $LSI$ ) do not exhibit clear bimodality at room temperature, as obtained from both classical and *ab-initio* MD ([ref](#)). However, the temperature dependence of  $P(Q_4)$  shows a different story.  $P(Q_4)$  is strongly peaked around  $Q_4 \approx .8$  at low temperature. As the temperature is raised, a peak around  $Q_4 \approx .5$  appears. At high temperatures the distribution becomes broad, and arguably can be characterized as bimodal. (The best calculations of this come from [Sedlmeier, et al.](#), but the bimodality is also mentioned in the original  $Q_4$  paper by [Kumar & Stanley, 2009](#)). When energy minimization is run on water structures, one obtains so-called "inherent" structures. These inherent structures exhibit a *clearly* bimodal distribution of  $Q_4$  even when derived from simulations of room temperature water([ref](#)) .

However, it is a mistake to conclude on the basis of either SAXS, a bimodal  $P(Q_4)$  distribution, or inherent structures that there are clearly delineated HDL/LDL domains in room temperature water. [Sedlmeier et al.](#) show that  $Q_4$ - $Q_4$  correlations do not extend beyond 6 Angstroms, or the 2nd H-bonding shell. Furthermore, they note that the correlation between  $Q_4$  and local density is rather small.

What then causes the enhancement at small  $q$ , corresponding to nanometer-scale wavelengths? In their [2010 article in PNAS](#), Clark, Hura, Teixeira, Soper, and Teresa Head-Gordon summarize their findings from simulation and experiment as follows:



*The increase in  $S(q)$  at small angle is due to the normal density fluctuations which arise from stochastic processes in a single component fluid. The tetrahedral network forming TIP4P-Ew model of water qualitatively reproduces the trend in  $S(q)$  at ambient conditions and yields the same correlation lengths arrived at by experiment. An increase in  $S(q)$  at small angle is due to a payoff between attractive and repulsive intermolecular interactions that are completely consistent with a unimodal density.*

In my view neither the idealized picture of HDL/LDL domains or the view of stochastic density fluctuations are fully satisfying when it comes to explaining the small  $k$  MD simulation tends to show that because of thermal fluctuations, room temperature water does not contain clearly resolved nanometer scale domains of HDL and LDL. Rather, it contains a hydrogen bond network that extends through all of space which is [severely distorted](#) in places, and may contain local inhomogeneities from hydrogen bond cooperativity. Overall though, the network has a largely tetrahedral character with a most molecules having 3 or 4 hydrogen bonds (avg 3.5-3.9). This type of overall homogeneity of water does not preclude the existence what we call 'polar nanoregions' in analogy to relaxor ferroelectrics. This is because polar ordering has more to do with the position of hydrogen atoms while structural ordering has more to do with the position of oxygen atoms. Ice XI and ice Ih have almost identical crystal structures, but ice XI is a ferroelectric because the hydrogen atoms are ordered. Local domains of ice XI can and do exist in ice Ih, and something analogous can in principle happen in liquid water. Alternatively, polar ordering may be due to distortions in the hydrogen bond network and/or rotation of under-coordinated/interstitial molecules.

The extent and nature of inhomogeneities in room temperature water remains controversial. The [Dec. 2015 review](#) by Nilsson & Pettersson in *Nature Communications* does a good job defending the validity of the two-state approach through several lines of experimental evidence, but controversially invokes a picture of HDL/LDL domains even at room temperature. The accuracy of MD simulations can always be called into question, but no present day experiment can resolve the controversy about the structure of room temperature water, simply because there is no microscope that allows us to see structure as it extends over nanometers. All spectroscopic or scattering experiments involve an effective convolution or averaging over the entire bulk. Furthermore, the isosbestic points found in Raman and infrared spectra, which were [previously thought](#) to be clear evidence for two-state structure, have been called into question ([ref1](#), [ref2](#)).

We hope that our work can provide a new experimental window into water structure through the analysis of LO-TO splitting in the dielectric susceptibilities, as derived from experimental complex index of refraction data ( $n$  and  $k$ ). From solid state physics theory it is understood that LO-TO splitting arises from long-range Coulomb or dipole-dipole interactions. In crystals, very long wavelength ( $k \rightarrow 0$ ) longitudinal optical phonons create a macroscopic E-field which increases their frequency relative to their transverse counterparts. Furthermore, as we discuss in our work, the degree of LO-TO splitting can in principle be related to structure. Intriguingly, we find an unexpected increase in the LO-TO splitting of the librational modes as temperature is increased.

### Further implications

In biophysics, the results indicate that a new class of water-mediated protein-protein interactions may be possible. Recent work has shown dynamical coupling between proteins

and surrounding water molecules ([Ebbinghaus 2007](#)), but the physical extent of this coupling is not very well understood. Currently this coupling is only being studied at low frequencies ( $< 33 \text{ cm}^{-1}$ ) ( $< 1 \text{ THz}$ ), but our work indicates such coupling could also exist at much higher frequencies.

Additionally, by comparing several different simulation techniques, we find that the non-polarizable water models fail to capture the optical phonon-like modes at the OH-stretch frequency. This compliments our [previous work](#) where we showed other ways that polarizable models are more accurate than the more often used non-polarizable models.

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