

The H-bond network of liquid water supports propagating phonons

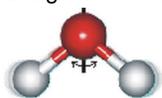
Daniel C. Elton M.-V. Fernández-Serra
Institute for Advanced Computational Science, Stony Brook University

Abstract

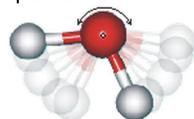
In this work we show that on subpicosecond time scales optical phonon modes can propagate through the H-bond network of water over distances of up to two nanometers. Using molecular dynamics simulation we find propagating optical phonons in the librational and OH stretching bands. Both of these phonons exhibit longitudinal-transverse splitting at $k = 0$, indicating the presence of long range dipole-dipole interaction. Since such splitting is intimately connected to structure, our analysis opens the door for new insights into how the structure of water changes with temperature. Our results also explain a previously unnoticed discrepancy one encounters when comparing the librational peaks found in Raman spectra with those in infrared and dielectric spectra. Previously the three librational peaks in Raman spectra were assigned to the librations of single molecules. Our results indicate these peaks are better understood as a transverse phonon, the wagging libration, and a longitudinal phonon.

The problem

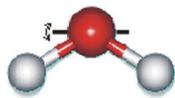
- We have found a previously unrecognized inconsistency between the peaks found in the librational region ($350 - 1000 \text{ cm}^{-1}$) of dielectric and Raman spectra for liquid water.
- Dielectric and IR spectra show 2 peaks, while Raman spectra shows 3 (see right)
- The previous assignment to the 3 Raman peaks was:



L1 = "twisting"



L2 = "rocking"
IR active



L3 = "wagging"
IR active

- However, the two IR active modes (rocking & wagging) do not show up in dielectric / IR spectra. Instead, peaks appear in the vicinity of L1 and L2

The solution

- We propose that L1 is actually a transverse optical phonon, while L3 is a longitudinal optical phonon.
- To show that L3 is a longitudinal mode, we look at the longitudinal dielectric susceptibility:

$$\chi_L(\omega) = 1 - \frac{1}{\epsilon(\omega)}$$

- A peak appears in the longitudinal susceptibility near where L3 is in the Raman spectra.

Longitudinal-transverse (LO-TO) frequency splitting

- From experimental dielectric data, we show LO-TO splitting exists in both the librational ($350 - 1000 \text{ cm}^{-1}$) band and O-H stretching band ($3000 - 3700 \text{ cm}^{-1}$) (see figure to right)
- LO-TO splitting is related to structure via:

$$\omega_L^2 - \omega_T^2 = \frac{4\pi C}{3v} \left(\frac{\partial \mu}{\partial Q_k} \right)^2$$

- Here v is the volume per unit cell, Q is the normal mode, and C is a factor which depends on structure (for a cubic structure, $C = 1$)
- LO-TO splitting provides a novel probe into changes in the local structure of the liquid with temperature

Molecular dynamics simulation

- To show that the modes are propagating phonon modes, we analyze the k -dependent dielectric susceptibility.
- We study three models:

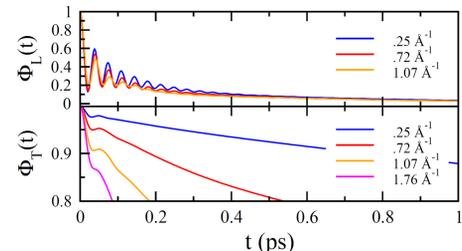
TIP4P/ε - a rigid model

TIP4P/2005f - a flexible model

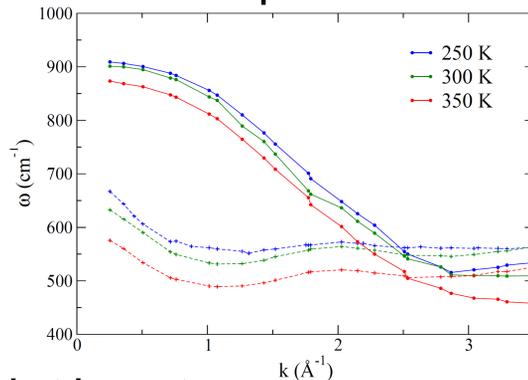
TTM3F - an *ab-initio* based polarizable model

- The librational modes are highly underdamped and are dispersive, indicating propagation.
- Important differences between the polarizable model TTM3F and TIP4P/2005f are observed in the OH-stretching band. TTM3F exhibits dispersion and LO-TO splitting in the OH stretch band, while TIP4P/2005f does not.

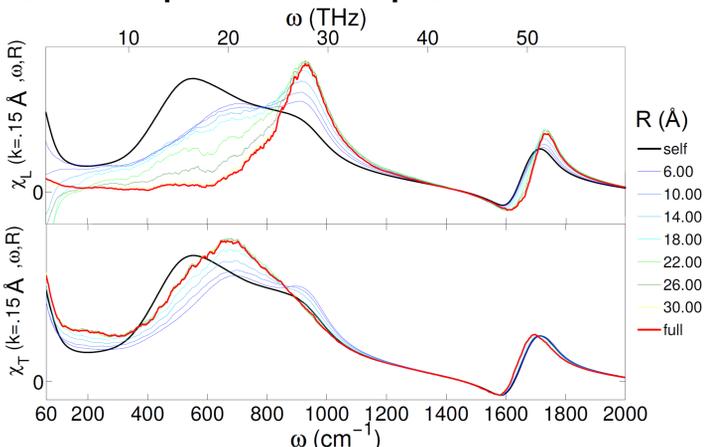
Polarization—polarization time correlation functions for TIP4P/ε



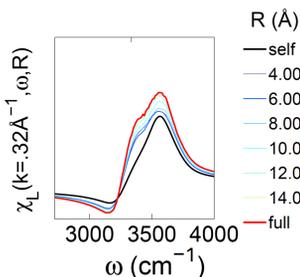
Phonon-like dispersion curves



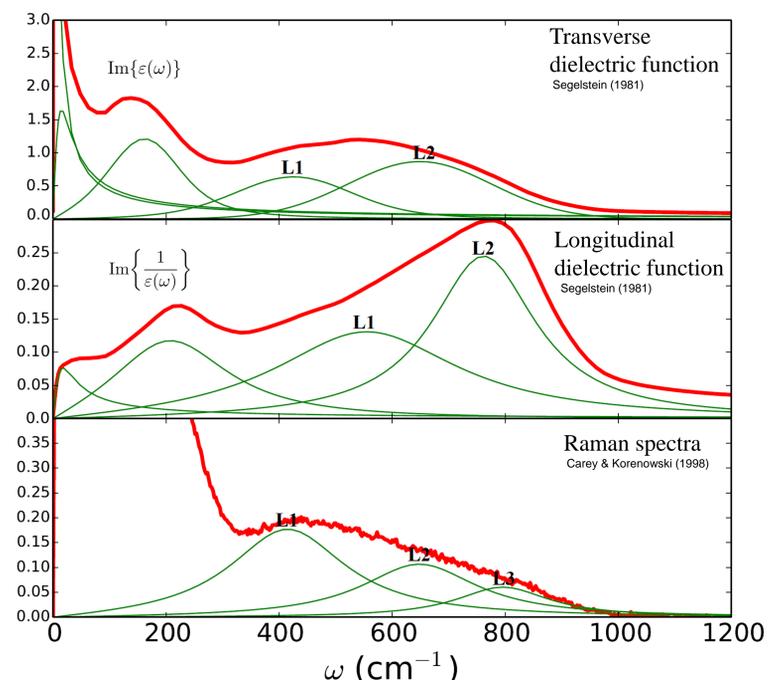
Distance-dependent decomposition of the dielectric spectra



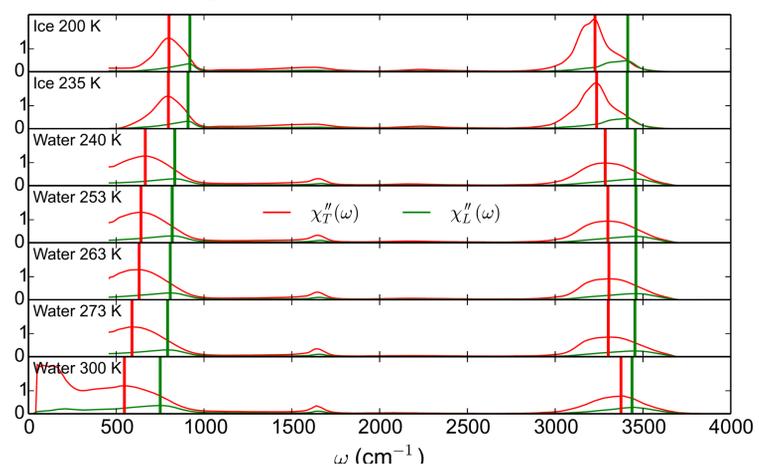
- MD simulation with TIP4P/2005F (above) in a large (4nm) box show contributions up to 2nm



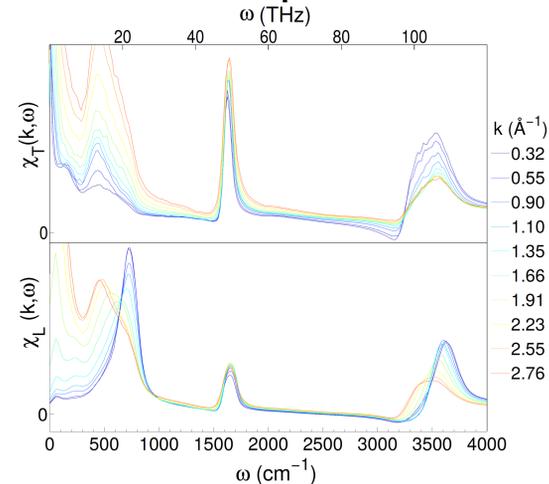
- MD simulation with TTM3F shows long-range contributions in the stretching band. The introduction of polarization allows for long range intermolecular coupling of the OH stretch vibrations.



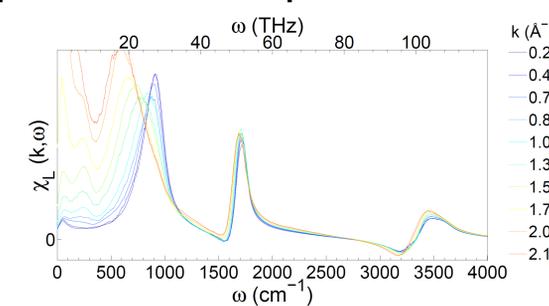
LO-TO splitting derived from expt. data¹



k -dependent dielectric spectra for TTM3F



k -dependent dielectric spectra for TIP4P/2005f



Our publications

- <http://arxiv.org/abs/1507.06363>

Elton, D. C. and Fernández-Serra, M.-V. "Long range optical phonons in liquid water" (under review) (2015)

- <http://arxiv.org/abs/1401.5090>

Elton, D. C. and Fernández-Serra, M.-V. "Polar nanoregions in water - a study of the dielectric properties of TIP4P/2005, TIP4P/2005f and TTM3F" *J. Chem. Phys.* **140**, 124504 (2014)

- blog: www.moreisdifferent.com
- twitter @moreisdifferent
- group webpage: <http://mini.physics.sunysb.edu/~marivi/>

Refs:
1.) Zaslavsky, et al. (2005) *J. Phys. Chem. A.* **109**, 2760.
2.) Carey, D. M & Korenowski, G. M. (1998) *J. Chem. Phys.* **108**, 2669–2675.

This work was partially supported by DOE Award No. DE-FG02-09ER16052 (D.E) and by DOE Early Career Award No. DE-SC0003871 (M.V.F.S.).

