

An introduction to the water structure problem

Posted on January 21, 2016 by delton137 in [non-technical research](#)

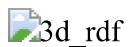
Although the macroscopic properties of water have been heavily studied, there are things we don't understand about this ubiquitous substance. In this post, I will provide an introduction to the problem of describing water's structure. At first glance, the idea of a liquid having structure seems preposterous. Indeed, liquids cannot maintain a structural arrangement of atoms like solids can. Instead, the atoms/molecules tumble past each other in constant state of motion. This allows for the defining property of the liquid state – the ability to fill a container.

However, one can talk about an average local structure in the following sense – if you were to sit on a water molecule's oxygen atom and observe where other molecules are around you, over time you would notice that the nearest neighboring molecules tend to be in certain places. This average structure can be quantified in a radial distribution function, which shows the likelihood of observing other atoms at different distances r from a central atom:

 Example oxygen-oxygen radial distribution function, showing experimental data from x-ray diffraction and calculated from a simulation with the TTM3F model.

Example oxygen-oxygen radial distribution function, showing experimental data from x-ray diffraction and calculated from a simulation with the TTM3F model.

If the positions of atoms are completely random, then the RDF equals to 1. Where it is greater than 1, that indicates an average excess of molecules at that distance, and where it is less than 1 indicates a deficit. Note that by this measure, structure does not extend that far out – only 10 Angstroms (1 nanometer) at most. Looking at RDFs is by no means the end of the story, as we will see. For one thing, rdfs are spherically averaged. To get a more complete picture one can also make 3D plots. For instance, at the distance of $r = 2.8$ Angstroms:



3D plot from a *ab-initio* density functional theory simulation. The blue lobes show regions where there is a high probability of finding other water molecules. The distance corresponds to the hydrogen bond distance. The tetrahedral symmetry that comes from hydrogen bonding is very apparent.

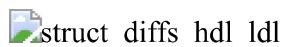
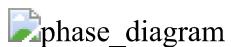


Figure from [here](<http://phys.scichina.com:8083/sciGe/EN/abstract/abstract508796.shtml>).

This plot was obtained from [quantum-mechanical simulations](#) performed by a previous grad student in our group, Jue Wang. In addition to doing the spherical averaging, RDFs do not tell us if the local structure varies through the liquid. For instance, there might be regions where each molecule has more hydrogen bonds on average, (more “ice-like”) which would cause the water in that region to have a lower density. Correspondingly, there might be regions where molecules have less hydrogen bonds, and more ‘interstitial’ molecules, which would cause a higher density. The idea that water may be inhomogeneous goes back to 1892, when W.K. Roentgen proposed that water contains a mixture of two structural motifs – “ice like” and “liquid like”. The idea helps explain many of the anomalies of water, such as the fact that water has a density maximum at 4 C. If you cool water below 4 C, it expands, which is highly anomalous. This could be explained though if the low density regions start to dominate below 4C.

what does the phase diagram of deeply supercooled water look like?

_ The debate about water structure dovetails with a debate about the low-temperature behaviour of water.



The regime where water can be supercooled and the different forms of amorphous (glassy) ice. Figure from [here.] (<http://phys.scichina.com:8083/sciGe/EN/abstract/abstract508796.shtml>)

Water can be easily supercooled down to -20 C. However around -45 C one runs into a hard limit, and water always freezes. There is much interest, however, in how about how water would behave if it could be supercooled even lower. This hypothetical part of the diagram is called the ‘no-mans land’.

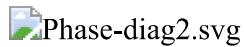
Interestingly, it is possible to create amorphous ice (sometimes also called glassy water). One way to do this is to cool water at an extremely rapid rate. If the cooling is done quickly enough, the water molecules don’t have time to freeze into ice, and they are trapped in a ‘glass’ which is technically a supercooled liquid state, but so cold that it behaves like a solid. Another way of making amorphous ice is by putting normal ice under high pressure.

At different pressures amorphous ice exists in two forms, low density (LDA) and high density (HDA), with a sharp phase transition between them. The video above shows what happens when you remove the pressure on HDA — it quickly converts to LDA.

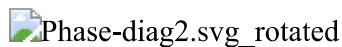
Now, you might think you could make supercooled water in the ‘no-mans land’ part of the phase diagram by heating up amorphous ice. Unfortunately, if you do this it turns into regular ice, because at higher temperatures the water molecules can move around more and adopt their preferred form.

There is a great debate in the scientific community about what the “phase” diagram is in the ‘no-mans land’. The term “phase” here is technically incorrect, because supercooled water is not a true thermodynamic phase, rather it is a metastable state. In any case, in a seminal 1992 *Nature* paper it was proposed that at some point in the no-mans land there is a second order critical point.

To understand what a 2nd order critical point is and why this would be important for room temperature water, consider the phase diagram of water shown in Chemistry 101 and Physics 101 textbooks:



Now let's flip it and rotate it so that pressure is on the x-axis and temperature is on the y-axis, so we can compare to our previous diagram:



The blue line shows the transition between liquid and gas. The red point at the top of this line is an example of a 2nd order critical point. Above this point, there is no sharp distinction between liquid and gas. Water above the critical point is called 'supercritical'. In super-critical water there are very large density fluctuations (inhomogeneities!).

Similarly, if a 2nd order critical point exists in the no-mans land between LDA and HDA, then liquid water should contain density fluctuations between HDL (high density liquid) and LDL (low density liquid).

Another diagram has been proposed though, called the '[singularity free](#)' version, and there is great debate about how to prove which picture is correct currently raging in the scientific community, which I don't have space to go into here. Many scientists like the concept of a critical point in the no-mans land, though, because it helps explain many strange anomalies observed in studies of supercooled water. Many of the properties of supercooled water, such as its compressibility, anomalously start to increase when water is supercooled and follow a trajectory that would [lead to a singularity](#) if a low enough temperature could be reached.

Is room temperature water homogeneous or inhomogeneous?

During the 80's and 90's there was also intense debate between experimentalists about how many H-bonds water molecules have. By the early 2000's, most scientists had reached a consensus that the

average number was around 3.5, that the H-bond network filled all of space and was mostly tetrahedral, and that density inhomogeneities were small at room temperature. A 2004 x-ray scattering experimentalists challenged this view by proposing that water contains many molecules with only 2 hydrogen bonds which are connected in long chains. This was [debated for some time](#) and is now largely believed to be ill-founded.

A greater challenge, still being discussed today, came with the publication of “[The inhomogeneous structure of water at ambient conditions](#)” by Huang, Nilsson, et al. in 2009. Their argument largely rests on their interpretation of small angle X-ray scattering (SAXS) data, which probes changes at long wavelengths, on the order of nanometers. They find that at long wavelengths there is an unexpected increase in the scattering of x-rays. The authors tried to reproduce this result by doing a molecular dynamics simulation and were unable to. Their implication was that molecular dynamics simulations can not be trusted to settle the debate about the structure of water. However, such things from simulation is very computationally expensive. Later simulations by [Sedlmeier, Horinek, and Netz](#) that used a better calculation method did recover the excess response.

What molecular dynamics simulations show

Molecular dynamics simulations with the most optimized models (which have names like TIP4P/2005f) do show the co-existence of clearly defined HDL-like and LDL-like domains at very low temperature. For instance, [Overduin and Patey](#) simulated at the chilly temperature of 175 K, in a long box rectangular box with dimensions 12nm x 3 x 3nm:



Taken from [Overduin & Patey, J. Chem. Phys. 143, 094504 (2015)]
(<http://scitation.aip.org/content/aip/journal/jcp/143/9/10.1063/1.4929787>)

The top panel shows where molecules identified as “ice-like” are, in red. The bottom panel shows differences in density, with regions with lower density than average (ice-like) also shown in red. The x-axis represents time. Notice that there is switching between the two types of local structure with a timescale on the order of microseconds (1000 nanoseconds). Such switching back and forth was observed in other simulation work that simulated a smaller box of [supercooled water for several microseconds](#).

While this is neat, simulations do not show any such heterogeneity in room temperature water.(ref) However, one can look at the distribution of the parameter Q4, which measures tetrahedrality around

each molecule. If the nearest neighbors were like they are in ice (nearly perfectly tetrahedral) then Q4=1. If they are random, Q4=0. There is a distribution of Q4 found in room temperature water with a peak around 0.8. [Sedlmeier, el al.](#) found that correlations in Q4 do not extend beyond 6 Angstroms, or the 2nd H-bonding shell.

If not nanometer scale heterogeneity, then could cause the excess x-ray scattering Huang et al observed? In a [2010 article in PNAS](#), it was suggested that normal stochastic density fluctuations can also explore the data. In my view neither this picture or the idealized picture of HDL/LDL domains are fully satisfying explanations. Both effects may be at play.

The current view that is most consistent with the experimental data is that room temperature water contains a hydrogen bond network that extends through all of space which is [severely distorted](#) in places, and may contain local inhomogeneities. Overall the network has a largely tetrahedral character with a most molecules having 3 or 4 hydrogen bonds (avg 3.5-3.9). Our [Nature Communications paper](#) shows how optical phonons propagate through this network. This type of overall homogeneity does not preclude the existence what we have called '[polar nanoregions](#)'. This is because polar ordering has more to do with the relative orientations of the hydrogen atoms while structural ordering has more to do with the position of oxygen atoms.

The extent and nature of inhomogeneities in room temperature water remains controversial. A [Dec. 2015 Nature Communications review](#) by Nilsson & Pettersson in *Nature Communications* defends the validity of the two-state approach to understanding water 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. Our recent work, [discussed in my previous post](#), opens a new window into probing the local structure of water through the analysis of dielectric spectra, which we believe can bring more clarity to how water's local structure changes with temperature.

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4 years ago

Why H₂O Polarity is Variable

Reply

**JM**[James McGinn](#)

8 years ago

Ultimately the biggest issue preventing the resolution of the water structure problem is psychological, the tendency for humans to be aesthetically attracted to idealized notions. And, in this case, that manifests itself in this absurd notion that the structure of ice is the result of water molecules forming into a lattice. This notion was assumed back in the 1930's and persists despite the fact it has never been verified. It is believed. And it is a huge obstacle because it gives researchers the false belief that they can ignore what is actually the best evidence we will ever have to untangle the water structure problem, that being the evidence associated with the transition between liquid water and solid ice.

If researchers were forced to admit that the body of evidence associated with this

transition was not yet properly explained they would be forced to conclude that there must be some mechanism that is activating polarity over this transition. (Because without this there is no way to reconcile why and how this transition is so discrete and why and how there is such a sharp distinction between the hardness of ice and the fluidity of liquid water.) And this would force them to recognize that, therefore, polarity must be turned off (neutralized) in liquid water. And this would force them to seek out the mechanism that achieves this polarity neutralization in liquid water--which I've

[see more](#)

o o Reply 

JM James McGinn

8 years ago



Science is confused about water because they are confused about polarity. They see polarity as a function of "polar" bonds (a "polar" bond is a covalent bond that has an electronegativity difference). It's not that simple. Many molecules have "polar" bonds but are not polar (they are not dipoles). A polar molecule is asymmetrical in addition to having electronegativity differences. And where it really gets confusing is when you consider that with water (and only with water) symmetry is variable--AND ACTUALLY VARIES AS A CONSEQUENCE OF HYDROGEN BONDING!

In water polarity drops to zero when symmetry is achieved through coordinated tetrahedral bonds. The failure to comprehend this and its implications is the reason they are so perplexed by water and its many anomalies. For example, once you understand this it becomes immediately apparent why H₂O has its high heat capacity. Strangely, the professionals have no ability to grasp the importance of symmetry to polarity. They write paper after paper and do video after video that demonstrates their ignorance of the intricacies of polarity and then they make lists of water's anomalies, pretending they have explained something that they have not explained. The following paper tries to get beyond that same ground hog day, over and over again, glossing over, inability to grasp what is really happening at the molecular level that is so typical of the study of water:

<https://zenodo.org/record/3...>

o o Reply 



JM James McGinn

8 years ago

"Doing so is tough though, because any theory about water has to reproduce all of the properties of water that have been unambiguously determined over decades of research."

The problem is that few have the ability to distinguish between what is unambiguously determined and what appears to be unambiguously determined. So progress comes to a standstill, as we see now in water sciences. You yourself substantiate this by the fact that you are defending a model that has failed to resolve upwards of 70 anomalies. You should be eager to discard such a dismal failure of a model, but you are not. If that is not the definition of a pathological science I don't know what is.

I want to present you with a challenge, Daniel, to see if you can think outside the box--

to see if you have the intellectual fortitude to directly address new thinking. See if you can directly address what is stated here, without turning to your advisor:

[see more](#)

o o Reply 

JM James McGinn

8 years ago

" . . . any theory about water has to reproduce all of the properties of water that have been unambiguously determined over decades of research."

In your opinion is there anything ambiguous about the 70 plus anomalies that are associated with current theory?

o o Reply 

JM James McGinn

8 years ago

"I understand why you don't like the word "structure" . . ."

I think what I stated is very clear that my dispute is neither semantic nor aesthetic.

o o Reply 

JM James McGinn

8 years ago

D.E.: "However, one can talk about an average local structure in the following sense – if you were to sit on a water molecule's oxygen atom and observe where other molecules are around you, over time you would notice that the nearest neighboring molecules tend to be in certain places. This average structure can be quantified in a radial distribution function, which shows the likelihood of observing other atoms at different distances r from a central atom:"

J. M.: Like much of current thought on water, which draws upon and is additive to some of the worst thinking in climate sciences and other related sciences that pander to public sentiment, what you are stating here, Daniel, is spiritualistic, not scientific. It's regrettable that this kind of non-scientific thought has become so pervasive that no real, empirically driven, scientist has much of a chance of making progress.

You are erroneously equating arrangement to structure. This is a plainly invalid argument. You are asserting spiritualism as an explanation. And then you are hiding your spiritualistic explanation in sciencey sounding rhetoric like, "This average structure can be quantified in a radial distribution function, which shows the likelihood of observing other atoms at different distances r from a central atom:"

[see more](#)

o o Reply ↗

D **delton137** → James McGinn
8 years ago

I understand why you don't like the word "structure" being used, but the definition of "average (local) structure" I give is rigorous.

"97% of the people in science are just along for the ride." - I'm not sure about that. Most scientists I know are very critical thinkers. Everyone scientist wants to discover flaws in previous work or develop new, more accurate theories and models. Doing so is tough though, because any theory about water has to reproduce all of the properties of water that have been unambiguously determined over decades of research.

People come out with new ways of quantifying water structure & dynamics every year. Some are found to be useful for understanding water and some are not useful. In my previous paper we look at dipole-dipole coorelation functions, for instance. The framework of using RDFs is useful because RDFs can be easily measured from x-ray and neutron scattering experiments - that is why I discuss it here. Dipole-dipole correlation functions and other esoterica is hard get from experiment.

o o Reply ↗

JM **James McGinn**
8 years ago

"This was debated for some time and is now largely believed to be il-founded.

A greater challenge, still being discussed today, came with the publication of "The inhomogeneous structure of water at ambient conditions" by Huang, Nilsson, et al. in 2009."

The debate continues and will continue indefinitely as long as the paradigm assumes the following:

symmetric bonding = low density = structural strength (ice)

asymmetric bonding = high density = structural weakness (fluidity, low viscosity)

The correct relationship is the following;

symmetric bonding = high density = structural weakness (fluidity, low viscosity) = polarity neutralized

asymmetric bonding = low density = structural strength (ice) = polarity activated (de-neutralized)

Until you all get this relationship straight in your minds the data will continue to stir the water of the debate into indefinitely.

o o Reply ↗

D **delton137** → James McGinn
8 years ago

I think the view is as you say - more distorted structures (allowing high

density) have more asymmetry. I've never heard of there being a clear correspondance though.. and certainly not an expert on H-bonding.

What I do know is that quantum simulations of liquid water show there is significant charge asymmetry in H-bonds. This is important, because it can explain the "pre-edge" seen in X-ray scattering. The cause of the "pre-edge" has been source of controversy. It was originally proposed to be associated with 1D long chains of molecules in the liquid.

Thomas D. Kühne's work on the subject has been highly publicized. They show the pre-edge can be explained by the charge asymmetry.

<http://www.nature.com/ncomm...>

I see he has another paper on the same the subject. (I haven't read either)
<http://pubs.acs.org/doi/abs...>

I honestly do not really understand the details, (which get rather technical) only the high level overview. Incidentally, my adviser told me recently that her research from 2005 reached basically the same exact conclusion as Kuhne:

<http://arxiv.org/abs/cond-m...>

o o Reply ↗

JM James McGinn → delton137
8 years ago

If your ab initio contains some kind of fundamental flaw (either inclusionary or disclusionary or both) then the model you build is going to be mistaken and you aren't going to have any way of knowing. Collecting more data isn't going to reveal the flaw but will instead give you a false sense of confirming the validity of the previous model.

I'm continually amazed that so many who are involved in the study of water structure take H bonding for granted. When you fully comprehend how H₂O polarity is variable and not constant and how H bonds are the mechanisms thereof it changes everything, including ab initio.

I'm not exactly sure what the "pre-edge" issue is, but I suspect it is an artifact of the flaw or absence in your ab initio--also.

o o Reply ↗

JM James McGinn
8 years ago

" . . . there is no microscope that allows us to see structure as it extends over nanometers.

"Our recent work, discussed in my previous post, opens a new window into probing the local structure of water . . . "

You missed the significance of your own work, in my opinion. Your work demonstrates that this in-liquid-water structure (low density anomalies) indicates molecules literally

touching/attached to each other. I can't imagine you do not at least suspect this. But you can't bring yourself to admit/accept this because you know--rightly--that it conflicts with everything you've been taught. You are so determined to obediently comply with what everybody else thinks that it has even brought you to submit a plainly absurd explanations, the notion that if we just pretend 'arrangement' equates to 'structure' that we can pretend the current model makes sense.

The current model fails because it was constructed by people that didn't fully understand fundamental principles in chemistry, like electronegativity, symmetry, and the pivotal significance of the electron cloud, which is effected by proximity to positive hydrogen atoms in the same way regardless of whether the hydrogen atom is attached covalently or not.

Your model (the standard model) is nonsense not because the data is bad, but because the ab initio assumptions are tacked on based not on factors that are generally true of other molecules but not of H₂O. (In reality there is an inverse relationship between magnitude of the force of the charge and proximity of the hydrogen atom to the oxygen atom. This is a consequence of the fact that hydrogen atoms neutralize polarity.) And so, the correct way to interpret blue colored distributions in the model constructed by Jue Wang you would want to invert all of them relative to the molecule. Also, the molecules are generally much closer together (You've interpreted low and zero charges of your data as being at distance when in actuality it indicates closeness.)

But the factor that overrides all of this isn't so much a scientific factor as it is a human foible, the tendency of us humans to become religiously attached to idealized models, like this notion that ice involves a tetrahedrally coordinated lattice.

o o Reply ↗

JM James McGinn
8 years ago



Although the macroscopic properties of water have been heavily studied . . . At first glance, the idea of a liquid having structure seems preposterous.

I love the clarity of your writing and how you have framed the issue. Good start! . . . if you were to sit on a water molecule's oxygen atom and observe where other molecules are around you, . . .

This is very clearly explained. Only if there is a pattern would we be able to predict where another oxygen atom is located.

This average structure . . .

I have a problem referring to this as, "structure." I think it is "arrangement", not "structure". I understand your premise. You are asserting that structure does not necessarily imply or require that the molecules are actually touching. There is more to my objection than just semantics. And I do realize the issue you are trying to resolve. And I realize that this issue is bolstered with data--allegedly valid data. So I am sympathetic to why you would use the word 'structure'. I will explain why such special pleadings are not necessary with my model.

This plot was obtained from quantum-mechanical simulations performed by a previous grad student in our group, Jue Wang.

Excellent. Your explanation is crystal clear. I can see that this involves looking at it

[see more](#)

o o Reply ↗

JM James McGinn

8 years ago



This is an excellent blog post. I really appreciate the clarity of the thinking being presented here. I will be leaving a larger comment, putting a spin on it that further makes the case for my model, but I just wanted to pay a compliment for such an excellent post.

Regards,

James McGinn

o o Reply ↗

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