

Recent water myths

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Abstract: Recently, there have been a number of claims about the nature of water as a liquid that seem to contradict traditional views. The present paper takes a close look at two of these claims—namely, that water is not the tetrahedral network that it is traditionally regarded as but a chain-like liquid, and that water is intrinsically heterogeneous by nature—and attempts to make sense of them.

Keywords: chain structure; computer simulation; mixture models; neutron diffraction; water; X-ray absorption spectroscopy; X-ray diffraction; X-ray emission spectroscopy; X-ray Raman spectroscopy.

INTRODUCTION

Because it is so important in many different fields of science, water quite naturally attracts an enormous amount of research into its properties and the atom-scale origin of those properties, both in its pure state and in solutions of ions and molecules of all shapes and sizes. Homeopathy, for example, arises from the perceived ability of water to remember its structure around a dissolved entity long after that entity has disappeared, the so-called memory effect of water. Perhaps two of the more bizarre recent claims are that the structure of water is affected by relatively modest magnetic fields [1] and that the structure of water is altered by sunlight [2]. This change in the structure of water due to sunlight appears unlikely: in Britain, for example, the rain during the day is just as wet as the rain at night. In [3] it is stated that water is not the tetrahedral structure traditionally assumed, but consists of chains of water molecules. In [4] it is proposed that ambient water is intrinsically heterogeneous, consisting of a mixture of low- and high-density forms, an idea which has been proposed on many previous occasions for more than 100 years. Given all this often conflicting information, it is not surprising there is much confusion on the true state of water.

Perhaps one of the most surprising facts about water is that it is a liquid. All of the elements that surround oxygen in the periodic table have hydrides which are gases at ambient temperature and pressure, while hydrogen oxide is definitely a liquid with quite a low vapor pressure, ≈ 5 mbar. Even more difficult to comprehend is that while water is a liquid with marked “hydrogen” bonds between its constituent molecules, water hydrogen bonds are being formed and broken extremely rapidly, typically around 10^{12} times per second. The diffusion constant is also surprisingly large, around $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which means that after 1 s any given water molecule has on average moved about $44 \mu\text{m}$ from its starting position, corresponding to $\approx 150\,000$ molecular diameters. Therefore, whenever we attempt to develop a picture of water we have to keep in mind the extremely dynamic nature of the underlying water molecules that form this material. Based on these numbers, it is difficult to envisage how water can re-

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tain any memory of its previous state at the molecular level for more than a tiny fraction of 1 s, unless of course the water has been captured or enclosed by some entity which prevents it adopting its normal molecular motion. A marked slowing down of water is believed to occur near charged surfaces; for example, in the case of chromium and some other ions in solution, the rate of exchange of hydration water with surrounding water extends to days or even longer [5].

Beyond the factual properties of water lies another issue that relates as much to the scientific method in general, but which, due to the elevated position of water amongst the huge variety of topics studied by scientists, gains increasing importance in this case. This is the question of how do we interpret the data that we measure? Water has been studied scientifically by innumerable people for centuries, and while there is often a general consensus on what makes water the material that it is, detailed interpretations often differ quite markedly. For example, possibly one of the more contentious issues is whether water is truly a continuum liquid or whether in fact it exists as a heterogeneous mixture of two or more components. This topic will be discussed extensively later in this paper, but before we do that it is interesting to try to establish what exactly is meant by the continuum or two- or multi-state models of water. Here, the significant word is “model”. Without a model of some form or another, it is impossible to interpret a set of experimental data. That model can be precise and mathematical such as the Newton equations of motion, quantum theory, or Einstein’s theory of relativity, or it can be vague, notional, and ill-defined, something in our heads but not describable in precise mathematical terms. Models of water tend to fall into the latter category since water science is generally anything but precise.

An exception to this rule occurs in computer simulations of water. Here, starting from a functional form for the interaction between water molecules one can, at least in principle, solve the equations of motion, either classically or quantum mechanically, and so predict the quantities that might be measured in experiments on water. The model for the interaction will likely not include all the correct physics of the interaction, and there may be some questions about the computational method itself, but overall computer simulation, in the absence of exact analytic theories, is probably the closest we come to setting up a quantitative model for water. This fact was first realized in the early simulations of Barker and Watts [6] and Rahman and Stillinger [7] and has been repeated many times since for a very wide range of interaction potentials. The fact that a computer simulation is quantitative of course in no way implies it is an accurate representation of water, simply that, as in liquids generally, the derived structure and dynamics are likely consistent with the supplied interaction potential.

Since they are based on statistical mechanics principles, as a general rule computer simulation models of water tend to give rise to a continuum picture, which does not mean that the structure of water is everywhere the same, but simply that it varies continuously from one place to another. There are no demarked regions where one particular structure dominates clearly over others. In these models, the coordination number of each water molecule is in the range 4–5 near-neighbors on the average, with an approximately tetrahedral arrangement, again on average. However, the coordination numbers of individual molecules may vary anywhere in the range 2–7, often with highly distorted local arrangements.

On the other hand, so-called two-state or mixture models are not so readily describable in statistical mechanical terms. They typically assume [8] the pure liquid actually consists of a mixture of two liquids of different densities and structures. The properties of water are then obtained as a function of temperature or pressure by water molecules transferring from one liquid to the other as the temperature or pressure are varied. Ironically, at about the same time that the first computer simulation models of water appeared, Walrafen was stating categorically that the observed temperature dependence of the Raman stretch spectrum of water “provide strong support for the two-state model of water structure” [9].

The difficulty with mixture models is that while they may seem attractive to explain some properties they are difficult to reconcile with the highly statistical and diffusive nature of the water molecule, as alluded to in the first paragraph. If after 1 s a water molecule is already 150 000 molecular diameters away from its starting position, then any distinct structures that are formed must be extremely

short-lived. Moreover, assuming they involve a significant number of the local neighbors of any given water molecule, they would imply a degree of cooperativity between water molecules that is certainly not captured in the computer simulation models. Mixture models almost always leave out a crucial interaction in their description which is not mentioned, namely, if we have a mixture of two liquids, molecules in one liquid will interact not only with other molecules in the same liquid, but also with other molecules in the other liquid. The absence of a cross-correlation or interaction in mixture models makes them extremely difficult to describe in statistical mechanics terms. A negligible cross-term could only occur in the real system if the two states were really two macroscopically distinct liquids that did not interact with each other. So far there is no evidence that water is actually two separate liquids that do not interact. Yet the notion that water has an intrinsic heterogeneous, two-state, structure, which seemed to die away initially with the advent of computer simulation, has in the past decade or so has been resurrected, right up to the present day [3,4,8,10]. A recent account by Moore and Molinero [11] summarizes some of this material.

Behind this general discussion about the nature of liquid water lurks another discussion about the nature of hydrogen bonding in water. Traditionally, it is assumed that in the crystallographic view of ice, each water molecule is hydrogen-bonded to four neighboring water molecules in a tetrahedral arrangement, with two hydrogen bonds formed by the central molecule “donating” its two hydrogen atoms, and another two formed by the central molecule “accepting” hydrogen atoms from the neighbors. This picture gives rise to the Pauling ice rules [12] which state that there is exactly one hydrogen between each oxygen atom in the ice lattice, and it has proved very useful in explaining the residual entropy of ice. There is, however, a slight problem with this model, namely, the intramolecular angle H–O–H is believed to be (in the gas phase) $\sim 104.5^\circ$ [13] and not the 109.47° that would be required for each hydrogen by pointing directly toward a neighboring oxygen on a tetrahedral lattice. Estimates for the H–O–H angle in water and ice Ih vary [14–16], but are generally less than the ideal tetrahedral angle. Given the high proton mobility in ice [17], it would not come as a surprise, therefore, to discover that the number of hydrogen bonds per water molecule in ice at any instant was slightly less than four on average, even though the ice rules require this number to be exactly four. This “instantaneous” view of ice is perfectly compatible with the crystallographic view: on average, there will be one hydrogen between each oxygen, but at any instant it may not be exactly on the line joining each pair of oxygen atoms.

What happens to this hydrogen bonding in the liquid when ice melts? It has been established for some time [18] that the coordination number of water is greater than 4, meaning that the local order has to be more complicated than purely tetrahedral. Even so, computer modeling of the neutron diffraction data for water, which are sensitive to the hydrogen positions [19], suggest that the quasi-tetrahedral nature of the first coordination shell in water is retained, even when pressurized into the so-called “high-density liquid” region. This picture was completely consistent with what had been seen previously in computer simulations of water [20], even if some of the details might have been different. It came somewhat of a surprise, therefore, when in 2004 it was announced [3] on the basis of new X-ray absorption spectroscopy (XAS) and X-ray Raman spectroscopy (XRS) data from water that this conventional view of the liquid was incorrect, and that water should be regarded more as a chain-like material. How could such a radical departure from conventional thinking be entertained? Moreover, if this were true, why had no one seen this before? Was it likely that of the possibly hundreds of scientists who had studied water at the molecular level not one of them had noticed on the basis of their data that water structure was actually made up of chains of water molecules, and not a tetrahedral-like network as conventionally assumed?

It is not possible in the amount of space available to go into all the ramifications of this new claim, but there are some salient issues that will be addressed here.

THE INTERPRETATION OF XAS DATA FROM WATER

The X-ray absorption event is by any standard violent: a core electron is excited to the continuum, and energy dependence of this event is measured either directly or indirectly via X-ray Raman scattering. The energy for this excitation is more than three orders of magnitude greater than the typical OH stretch frequency, but is assumed to occur so fast that the event is observed before it has had a chance to perturb the local surrounding water molecules. Undoubtedly, the XAS data reported in [3] are state of the art, but the question of what they mean is not so clear cut. The conclusion that water has typically only two strong hydrogen bonds was based on a phenomenological argument. Spectra were shown for bulk ice, and the ice surface, as well as liquid water and gas-phase water. The similarity between liquid water and the ice surface (where presumably many of the water-water hydrogen bonds are broken compared to bulk ice) spectra was the primary rationale that was used to argue for a much reduced hydrogen-bonding regime in bulk water. In particular, it is seen that the XAS spectrum has a strong “post-edge” feature, attributed to tetrahedral bonding, while liquid water and the surface of ice has a stronger “main edge”. In addition, the “pre-edge” feature in water and surface ice is much more marked than for bulk ice. The argument was further supplemented with density functional theory (DFT) calculations using the half-core hole (HCH) approximation to the core-hole potential. By selecting specific water molecule coordinations with a high degree of broken hydrogen bonds, the researchers were able to reproduce their experimental data quite accurately, and so, on the basis of these two results, concluded that the majority of water molecules in the liquid had only two hydrogen bonds, leading to a chain-like structure. Subsequently, they argued that the HCH potential they use in the DFT calculations was superior to the full core-hole potential (FCH) advocated by other researchers [21].

Further experimental work followed. Tse [22] investigated the XRS of water, crystalline ice, and low- and high-density amorphous ices (LDA, HDA, respectively) and found close agreement between LDA and crystalline ice on the one hand (both have a strong post-edge feature), and liquid water and HDA on the other (both have strong pre- and main-edge features), suggesting the local geometry in water might be similar to that found in HDA and different from that found in LDA and crystalline ice. The XAS spectra for concentrated monovalent ionic aqueous solutions [23,24] shows enhanced main-edge intensity compared to pure water. Even detailed comparison of heavy and light water [25] shows slightly enhanced post-edge intensity in heavy water compared to light water.

How do all these results compare with existing structural interpretations of the same states? In the LDA/HDA comparison, it was established [26] that the primary distinction in local order between these two polymorphs is not the tetrahedral nature of the local coordination shell, which was similar for both cases, but the presence of a “lynch pin” molecule, not hydrogen-bonded to the central molecule, that is present in the first coordination shell of HDA but absent in LDA. Similarly, in aqueous monovalent ionic solutions [27], the most notable feature with increasing ionic concentration is the movement of the second water coordination peak toward the first. (In [23], XAS data are also shown for trivalent AlCl_3 solutions, where the trend is apparently for more tetrahedrality, but there are no corresponding diffraction data to compare with in this case.) Even in the case of the light water/heavy water comparison [28] the main structural feature was the slight washing out of the second coordination peak in H_2O compared to D_2O . Thus, there does seem to be a correlation between the relative heights of the main- and post-edge peaks in the XAS/XRS spectra, and the nature of the coordination of the first water shell together with the proximity of the second. For those liquids for which the second shell has more significant overlap with the first, these same liquids show the stronger main-edge intensity compared to the post-edge intensity.

Notwithstanding the controversy about the correct theoretical interpretation of the XAS data, there is a strong indication here that interpreting the XAS spectra in terms of water chains is not supported by other evidence, and that a more rational interpretation of these data would be in terms of the presence or absence of non-bonded molecules in the first coordination shell. Such an interpretation does not entail the view of water as a chain-like structure espoused by [3]. Indeed, precisely this view has

been expressed on the basis of a new FCH calculation [29]. It is interesting also that in independent work that appeared in 2002 [30] it is claimed via X-ray emission spectroscopy (XES) on water that the post-edge intensity in the XAS is indeed dominated by 4-bonded water molecules, but the pre-edge intensity is determined from primarily 3-bonded water molecules (called D-ASYM in that paper), although there was no speculation on the relative population frequency of the two species. This seems to be at odds with the claim that “most molecules are in 2-hydrogen bonded configurations...” based on the more recent XAS/XRS data [3]. Given the radically different nature of the two claims, it seems strange the *Science* paper of 2004 does not refer to the Guo [30] work. (Note that a later paper [31] does cite the 2002 work, but does not refer to the different conclusions.)

Following the publication of the idea that water was made up of chains, and the significant discussions that followed, I developed an “asymmetric” model of water which made the unphysical assumption that the two protons on the water molecule were distinguishable [32]. An electronic charge was placed on one proton, but not the other, and this gave rise to a structure that largely met the 2-hydrogen bond criterion described in [3]. The value of the charges was adjusted to give a reasonable configurational energy. It was found that a moderately acceptable, although not perfect, fit to the existing neutron and X-ray data could be made using this model. Not surprisingly, given its unphysical hypothesis, this work was criticized [33], but it did raise the serious question of what can and cannot be claimed on the basis of diffraction data from water. This matter was taken up in subsequent publications [34,35], leading to the claim that “Diffraction and IR(infra-red)/Raman data do not prove tetrahedral water” [35]. Equally, I suppose one could argue that diffraction and IR/Raman data do not disprove water is tetrahedral.

Here again, however, it could be argued that the reporting of this work has left out an important observation. As part of their study of calculating the XAS and IR spectra for water from the different structural models, Leetmaa et al. [34] calculate the XAS spectra from both my symmetric and asymmetric models. The differences between the two calculations were rather marginal (see Fig. 1 of [34]), despite the fact that the underlying local structures in the two models were radically different. The conclusion in [34] is that the structural analysis of X-ray and neutron diffraction data contains “unphysical structures” that are allowed by the diffraction data. This glosses over the obvious point that the very same theoretical methods that were used in [3] to claim that water has only two hydrogen bonds could not distinguish between two models of water, one of which had ~4 hydrogen bonds per molecule, and the other ~2 hydrogen bonds per molecule. A more logical conclusion might have been either that XAS data were not overly sensitive to the local geometry of water molecules (which, given the above observations, seems unlikely) or that the methods used to calculate XAS spectra from molecular distributions were not yet accurate enough to make the claims that were being made. The subsequent paper [35] did not really shed any more light on the matter, but, if anything, reinforced the view that current methods for calculating the XAS spectrum for water were inadequate for giving quantitatively useful results. It also needs to be pointed out that in order to get these non-tetrahedral models of water one has to apply highly restrictive constraints on the local molecular configuration by artificially excluding or including specific structures (such as double donor (DD), single donor (SD), etc.) in the structure refinement, constraints that have yet to be defined in terms of any kind of realistic potential energy function. The tetrahedral model of water does not require these constraints, but typically arises from simple Coulomb charges on or near the water molecule atoms, combined with Lennard–Jones potentials to prevent atomic overlap and to model the attractive dispersion forces.

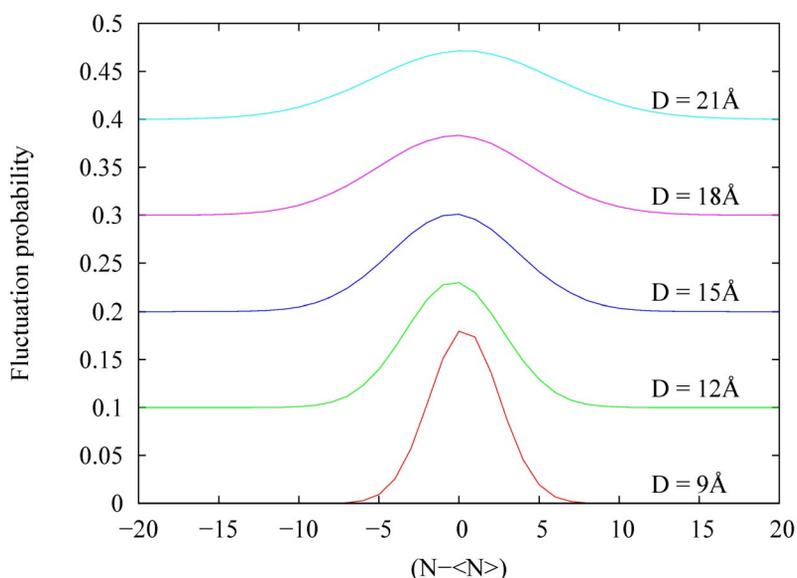


Fig. 1 Fluctuation probability for EPSR computer-simulated water [39] based on diffraction data as described in the text. The number N of molecules in cubic boxes of the specified dimension D are sampled, with the boxes being chosen 1000 times from random positions within the computer simulation box, and from more than 2000 different molecular configurations. The case shown corresponds to the “PCCP” simulation described in [39]. The results are plotted as a function of $N - \langle N \rangle$, where $\langle N \rangle$ is the average number of molecules in each box.

TWO-COMPONENT MODELS OF WATER

As already noted in the introduction, two-component models of water have been a recurring theme throughout the history of water research. They have been inferred from both structural [8] and spectroscopic [3,4,9,10] data. Yet, recent studies have argued that the claim for two-state behavior in water is not justified on the basis of either spectroscopic [36,37] or diffraction [38] data: in both cases continuum computer simulation models of water could be shown to give precisely the same “isosbestic” behavior that was previously used to claim two-state behavior.

To give an example of this, based on an idea originally developed by Hummer et al. [40], and using an empirical potential structure refinement (EPSR) of X-ray and neutron diffraction data as described in [39], I show in Fig. 1 the typical distribution of number fluctuations for a range of sampling volume sizes. It can be seen immediately that over all the sample sizes, the distribution of number fluctuations is closely Gaussian in nature and more importantly has a single mode, situated close to the expected number of molecules in each box. Moreover, it should also be noted that in the smallest box shown in this figure, in this case 9 Å, the number fluctuations can be up to $\sim \pm 7$ molecules. This corresponds to a density fluctuation of up to ± 0.0096 molecules per Å^3 , that is $\pm 29\%$ compared to the average water density of 0.0334 molecules per Å^3 . Hence, large density fluctuations are possible over this length scale in a stochastic system, but there is no evidence in these distributions for the bimodal distribution that might be expected if there were two distinct types of water structure present in the liquid.

It was, therefore, once again a surprise when it was claimed recently [4] on the basis of small-angle X-ray scattering (SAXS) data that water is in fact heterogeneous in nature. Here there was observed a small rise in the SAXS structure factor, and this was taken, together with the XAS/XES data, to imply an inhomogeneous structure. However, it has to be pointed out that the behavior of the structure factor $S(Q)$ at low wave vector change, Q , cannot be used to directly infer structural heterogeneities. In 1971, Weeks, Chandler, and Andersen [41] studied a simple repulsive plus dispersive force

law and showed unequivocally that even with this very simple force law between atoms, the structure factor could rise at low Q , depending on the density and relative strength of repulsive vs. attractive forces. The same point is illustrated in Fig. 2. I have calculated the structure factor and density fluctuations for a Lennard–Jones fluid at a point well away from the critical point of this fluid [42]. Despite a marked rise in the structure factor at low Q , the corresponding number fluctuations remain steadfastly unimodal and Gaussian-like. Indeed, the number fluctuations (not shown here) remain unimodal all the way down to the critical point, and only become bimodal once the temperature has dropped below the critical point [42].

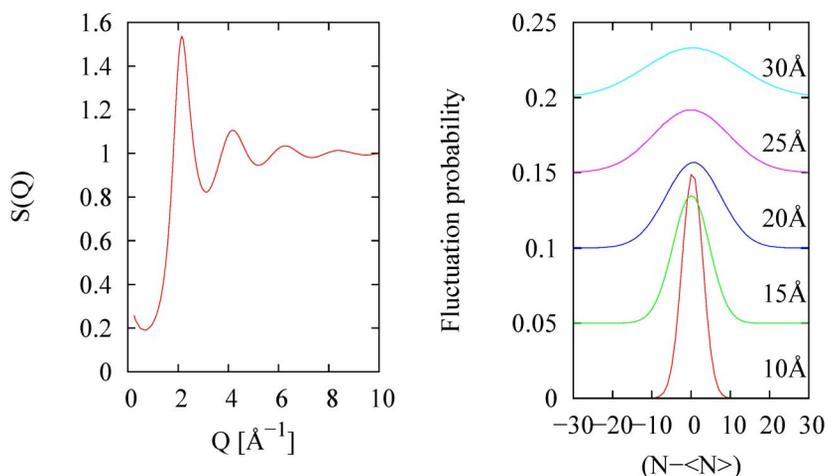


Fig. 2 Structure factor (left) and density fluctuations (right) for a Lennard–Jones fluid at a density of 1.8 times the critical density and 1.365 times the critical temperature [42].

Hence, a rise in the low Q structure factor does not by itself mean there must necessarily be density heterogeneities in the fluid. On the other hand, such a rise equally does not rule out such heterogeneities, and in [4] it is argued that the combination of SAXS and XRS/XES data gives support for the notion of a two-state structure for water. To examine this matter further, I have developed a simple hard-sphere model for structural heterogeneities.

A SIMPLE HARD-SPHERE MODEL FOR STRUCTURAL HETEROGENEITIES

The model is based on an earlier analysis [43] of the so-called “excluded volume” effects which occur when solute particles are dissolved in water, or when water is in confined geometry [44]. Referring to Section 3.2 of [43], we suppose the liquid consists of two components, a uniform component of density ρ into which are inserted uniform, mono-disperse, nonoverlapping spheres of internal density $(1 + f)\rho$ so that f represents the fractional difference in density inside the spheres compared to outside. The average atom density in the system is thus given by $\bar{\rho} = (1 + fx)\rho$ where x is the volume fraction of the spheres in the whole system. Thus, if the spheres occur with a number density ρ_c and diameter σ the

volume fraction is $x = \frac{\rho_c \pi \sigma^3}{6}$. For the purposes of this demonstration, we ignore the internal structure of both spheres and surrounding fluid and treat them both as uniform. Hence, any density fluctuations that occur in this model will arise purely from the heterogeneities caused by the density difference between the two components. If $f = 0$, then the $Q = 0$ limit of the structure factor will go to that of the ideal gas, namely, unity.

The radial distribution function for this model system can be shown to be eq. 20 in [43]:

$$g(r) = 1 + \frac{f^2 x}{(1 + fx)^2} g_p(r) + \frac{(fx)^2}{(1 + fx)^2} \frac{1}{v_p} \int d\mathbf{u} [g_c(\mathbf{r} - \mathbf{u}) - 1] g_p(\mathbf{u}) \quad (1)$$

where $v_p = \pi\sigma^3/6$ is the volume of the spheres

$$g_p(r) = \begin{cases} 1 - \frac{3}{2} \frac{r}{\sigma} + \frac{1}{2} \left(\frac{r}{\sigma}\right)^3 & r < \sigma \\ 0 & r \geq \sigma \end{cases} \quad (2)$$

is the radial distribution function for a solid sphere, and $g_c(r)$ is the radial distribution function for the sphere centers. With these definitions, and making use of the fact that the Fourier transform of a convolution is equal to the product of the transforms, the corresponding structure factor is given by

$$\begin{aligned} S(Q) &= 1 + \bar{\rho} \int d\mathbf{r} [g(\mathbf{r}) - 1] \exp(i\mathbf{Q} \cdot \mathbf{r}) \\ &= 1 + \frac{f^2 x}{(1 + fx)^2} \bar{\rho} v_p S_c(Q) S_p(Q) \end{aligned} \quad (3)$$

where

$$S_c(Q) = 1 + \rho_c \int d\mathbf{r} [g_c(\mathbf{r}) - 1] \exp(i\mathbf{Q} \cdot \mathbf{r}) \quad (4)$$

and

$$S_p(Q) = \frac{1}{v_p} \int d\mathbf{r} g_p(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) = 9 \left(\frac{\sin QR - QR \cos QR}{(QR)^3} \right)^2 \quad (5)$$

with $R = \sigma/2$. Therefore, the term

$$S_{\text{excess}}(Q) = S(Q) - 1 = \frac{f^2 x}{(1 + fx)^2} \bar{\rho} v_p S_c(Q) S_p(Q) \quad (6)$$

represents the perturbation to the structure factor due to the density inhomogeneities that have been introduced.

We note that for the likely size of heterogeneities that might occur in a real system (e.g., diameter $> 10 \text{ \AA}$) the form factor $S_p(Q)$ decays rapidly with increasing Q so this perturbation will only appear in the low Q region. The perturbation is dependent on several factors, namely, the relative density difference inside and outside of the spheres, f , the sphere packing fraction, x , the volume of the spheres, v_p , and the $Q = 0$ limit of the centers structure factor (which in turn depends on x). Hence, even if $S(0)$ and v_p are claimed to be measured as in [4], this does not allow us to assign unique values to either f or x .

Figure 3 shows the calculation of $S_{\text{excess}}(Q)$ for a sphere packing fraction $x = 0.1$ for several fractional density differences, assuming the same mean number density as for ambient water. The centers correlation function $g_c(r)$ was calculated within the Percus–Yevick formalism for hard spheres [45]. According to Fig. 3 of [4], the amplitude of this excess structure factor in the real liquid is of order ~ 0.02 . It can be seen that the calculated excess reaches this value when the density difference is of order 10 %—that is with a sphere packing fraction of 0.1.

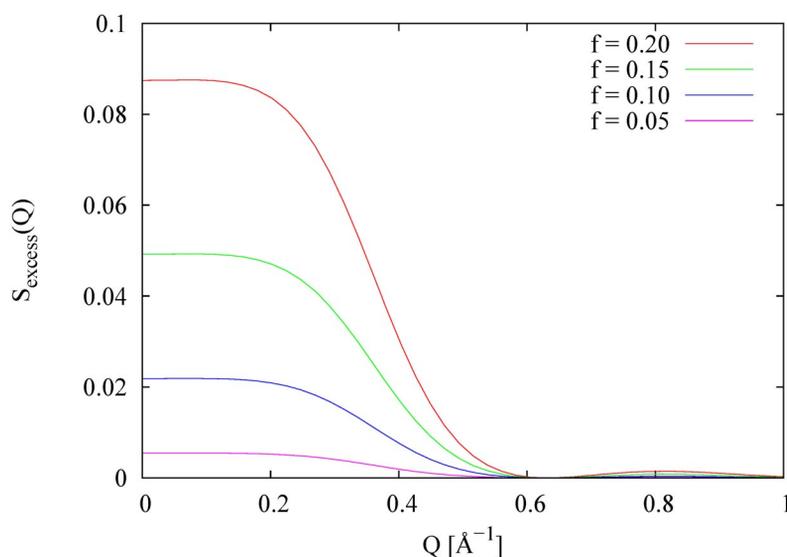


Fig. 3 Excess low Q structure factor caused by density heterogeneities as calculated from eq. 6 assuming a sphere packing fraction of $x = 0.1$ for various density difference fractions, f , in the range 0.05–0.2. The sphere diameter is 14 Å, and the assumed mean atomic number density is 0.0334 molecules/Å³.

On the other hand, Fig. 4 shows the calculated excess structure factor with the fractional density difference set at 0.1, while varying the sphere packing fraction. As the sphere packing fraction increases, so the structure factor associated with the sphere–sphere correlation function, with a peak near 0.4 Å⁻¹, becomes much more prominent, while the $Q = 0$ limit of $S(Q)$ actually falls. The complete absence of such a correlation peak in the measured SAXS data from water [4] means either that the dif-

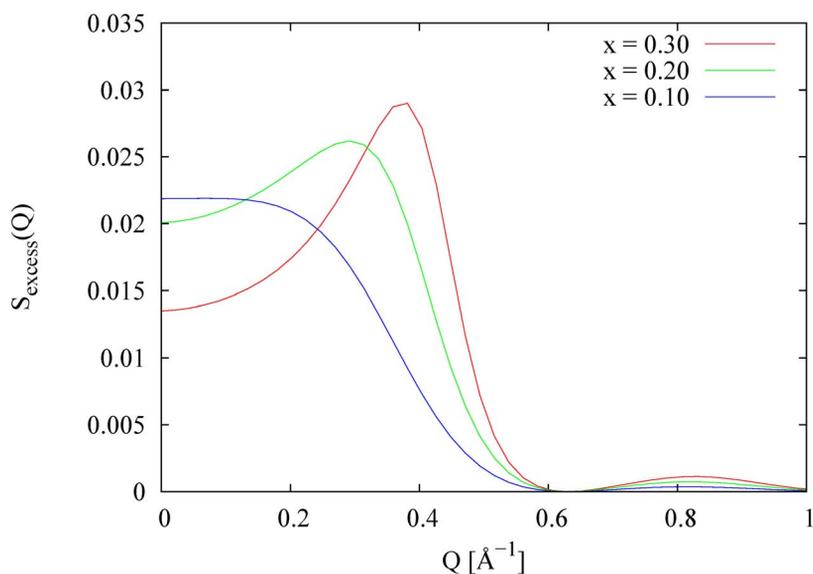


Fig. 4 Excess low Q structure factor caused by density heterogeneities as calculated from eq. 6 assuming a density difference fraction, $f = 0.1$, for various sphere packing fractions, x , in the range 0.1–0.3. Other parameters as for Fig. 3.

ferent density regions are highly disperse, having a broad range of shapes and sizes, or occur at not more than a 10 % packing fraction.

Comparing these two figures with what is measured [4] in the experiment, the conclusion is that if density heterogeneities do occur in water they occur either with a relatively low density difference of around 10 % and at a relatively low packing fraction also around 10 %, or else they must be highly disperse with a range of shapes and sizes. It would be straightforward to generalize the present model for such polydispersity and so improve the shape of the calculated low Q behavior compared to the experiment. But the point is that as the polydispersity becomes larger, so it becomes increasingly impossible to distinguish this situation of density heterogeneities from the situation occurring in any liquid, namely, that the natural stochastic fluctuations of density in water are in any case likely to be quite large. Certainly, to claim that the SAXS data give categorical evidence for a heterogeneous structure is erroneous.

DISCUSSION AND CONCLUSION

There are many other recently reported strange behaviors in water. Two of the more notable of these are mentioned in the abstract [1,2] but will not be discussed further here for lack of space. Instead, the present analysis has focused on recent claims that water is made up of chains and that it also has a heterogeneous structure, because these claims appear to challenge traditional thinking rather dramatically. These claims were accompanied by substantial media hype—see, for example, <<http://news.stanford.edu/news/2009/august10/watermolecule-mysteries-081109.html>>, where we are told: “These experiments suggested that the textbook model of water at ambient conditions is incorrect and that, unexpectedly, two distinct structures, either very disordered or very tetrahedral, exist no matter what the temperature.” In fact, as outlined in the previous sections, the evidence for either of these claims is insubstantial at best.

The claim that water is chain-like was made on the basis of a series of phenomenological extrapolations from measurements on specific systems such as gas-phase water, bulk crystalline ice, surface ice, and so on, accompanied by computed spectra using methods about which there is certainly no consensus, and indeed a lot of criticism, as to their correctness. The phenomenology of the XAS/XRS data is that water and HDA have similar spectra, and are different from LDA and ice, which are also similar. Equally monovalent ions can have a similar effect on the XAS data as the observed change from LDA to HDA in that the main-edge intensity often grows at the expense of post-edge intensity as the ionic concentration increases. All these behaviors have one thing in common, namely, the increasing presence of non-bonded water molecules in or near the first (tetrahedrally coordinated) shell. Since both HDA and LDA have a tetrahedrally coordinated first shell as found in the diffraction experiments, there is therefore no need to invoke chains to explain these XAS/XRS spectra. What is needed is an accurate method of calculating the XAS/XRS spectra based on molecular models, and the consensus on how to do that is currently lacking, with claims and counter claims being made.

When the *Science* article was published in 2004 [3] it was presumably based on earlier accounts, [46,47]. However, by 2004 there had been at least three previous independent attempts at XRS/XES measurements on water [30,48,49]. These included the first XRS experiment on water [48] where analysis of the first peak in the XRS spectrum was avoided because of “1 the increasing importance of multiple scattering contributions as one approaches the absorption edge region combined with 2 the considerable difficulty in defining a reliable set of atomic potentials in which the electron scattering and atomic excitation processes take place.” The article then goes on to list other reasons why analysis of this peak might be unreliable, including the problem of how to deal with the core-hole excitation as already alluded to. The study by [49] does not make any statement about local configurations based on the measured data, but the XES study in 2002 [30] states that the pre- and main-edge regions are dominated by three-hydrogen bonded species. The fact that such previous results, which are clearly in con-

trast to the claims of [3], are not referred to or discussed in that paper, casts doubt on the primary claim by those authors that water typically has only two hydrogen bonds per molecule.

The claim that water is heterogeneous is by no means new, dating back more than 100 years, but it is not widely accepted because computational efforts to simulate water never find distinct heterogeneities. As with any liquid, substantial density fluctuations occur, particularly on the nm length scale, but it would be incorrect to categorize these as “heterogeneous” (see Figs. 1 and 2) since the distribution of number fluctuations remains unimodal in the liquid phase or above a critical point. Inevitably, we end up where we began, namely, with a picture of water molecules changing neighbors and diffusing away from their starting positions extremely rapidly, so preventing clear structural groupings of molecules from developing. If water really did consist of alternating patches of high- and low-density structures, then it would imply a degree of cooperativity between water molecules that has not been found either in experiment or in simulation. It would also probably not be consistent with the high rate of diffusion of water molecules. A simple hard-sphere model of these heterogeneities showed that the amplitude of any rise that might occur in the low Q region of the diffraction pattern would arise from the density difference between the two species, the volume of the species, the packing fraction, and the way the spheres were packed. Comparison between this model and the actual data showed that the real system would likely have to be highly disperse, meaning there would have to be a broad range of particle sizes, since there is no evidence of a definite correlation between species in the low Q data. (Compare Fig. 4 here with Fig. 1 of [4].) Such a heterogeneous model would in fact be indistinguishable from the stochastic number fluctuations that occur in any liquid, so why invent something (i.e., heterogeneities) when none are needed?

These controversies do, however, underline some of the fundamental limitations of the techniques used to look at water and similar fluids. The information extracted is usually highly derived, often requiring complex, heavily approximated calculations from a starting model consisting of atoms and molecules. The link between model and experiment is simpler and more direct for diffraction experiments, but here the lack of sensitivity of the data to the many-body correlations which really define water structure can make obtaining an unambiguous structural picture from the experiments difficult. It is to be hoped that as a result of analyzing each controversy as it arises, one day someone will develop a more accurate method of deriving the structural and dynamical information about water that we are seeking.

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