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On the microscopic structure of liquid water

Aurélien Perera

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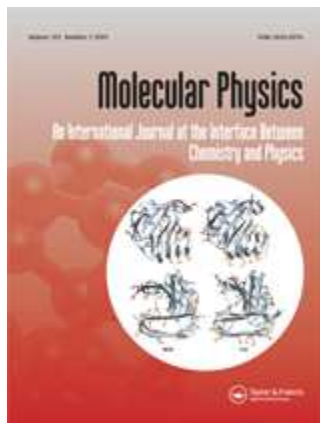
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On the microscopic structure of liquid water

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Manuscripts

Reply to the Referee's comments on revised manuscript TMPH-2011-0253

The Referee has made very explicit statements about the changes he wishes in the manuscript in points (2-6). I have complied to all of them in the second revision of the manuscript (see below in detailed answers). As to point (1), since it does not say explicitly what to change, I have just altered the points that the Referee mentions when the directive of changes could be guessed. I note that none of the points raised by the Referee concern the main points of the manuscript on the 3PS and subsequent finding. I therefore hope that these modifications will find satisfaction.

In what follows, I will address the changes I have made from (2) to (6), and come to point (1) at the end.

(2) *"The author continues to ignore the problem of stating that the peak heights (of the split peak feature in the structure factor)- which is an artefact of the normalization choice- means stronger scattering:*

"Being taller also means that the OH correlations are stronger, at long range, than the packing effects."

Please remove this statement. If the author prefers to ignore my request, then I suggest that the paper be rejected or sent to another reviewer."

I have removed this sentence from the manuscript.

(3) *"The author is not expert in the experimental uncertainties of neutron scattering data due to inelastic scattering in the region of 3A-1. Please remove sentence:*

"A closer look at the neutron SF reported in Ref 27 nevertheless reveals a small hump at $k \approx 3\text{\AA}^{-1}$, a weak sign of the H-bond ordering."

The incriminated sentence have been now removed.

(4) *"I do not agree with the summary of Guillot in 2002 (a reference 10 years out of date to current water models)*

"It is well acknowledged that polarisable force field model for water are generally speaking not as good as non-polarisable force fields. "

That work showed that some properties are better and some worse using polarization (again I emphasize a study done 10 years ago!) and that fixed charge FFs (10 years ago) were the same, not better or worse. That sentence should be deleted."

Even if the Guillot paper is now 10 years old, it has a very high citation index and seems to be a reference for many water experts in the community, from what I have personally gathered. Many things he says about polarisable force fields are still true I believe. Nevertheless, I have complied with the referee asking and removed this sentence from the manuscript.

(5) *"Reference on page 2 marked as "?""*

I thank the Referee for mentioning this glitch to me. I have corrected it now. The missing Reference is to Guillot [11].

(6) *"The following sentence is very unclear and needs to be restated so that readers can follow the authors's point:*

1
2 *"One suspects that this long range "ideality" is only apparent, and it hides canceling effects, but*
3 *which?" "*
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6 This sentence means to say that, if long range correlations beyond 10A are zero, then the effective
7 mean force potential is also zero in this range, which also means that particles do not interact and
8 therefore appear as "ideal" particles in this very range. However, this is certainly not true, and
9 some cancellation effects must be hiding behind this feature. I have now modified the first part of
10 this sentence according to what written above.
11

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13
14 **(1)** I find that the Referee is complaining now about material that were already present in the first
15 version of the manuscript, and about which he did not raise any comments in the first refereeing
16 part. Anyhow, I will break up the various points to ease the answers.
17

18
19 *"I find the introduction confusing as to what point the author is trying to make. It seems to involve a*
20 *mish mash of statements about local tetrahedral structure vs. mixture models. The author brings up*
21 *references to changing structure with temperature when his study is at room temperature. He*
22 *references the Huang et al study as if underlying heterogeneous structure and mixture models have*
23 *found experimental verification. "*
24

25
26 The only changes that were brought to the Introduction were based on the previous comments of the
27 Referee about the usefulness of the reference to Huang et al. [15-16] precisely. I could not find in
28 the text the statement(s) where I say that their claims have found experimental verifications. As to
29 the temperature dependence, it is to mention the evolution of the tetrahedral structure.

30 The purpose of the Introduction, as I wrote it initially, is very clear to me. It is all about to briefly
31 describe the state of matters about the tetrahedrality of water and the various hypothesis about the
32 underlying statistical structure of the liquid. I found this useful before I bring up the main finding of
33 this paper which is the 3PS. The description of the historical background may not be perfect in it
34 present form, but it does gives an overall idea of the past and current state of knowledge, in my
35 opinion.
36
37

38
39 *"I also don't believe that the water field is so naive as to base their analysis on "instantaneous*
40 *snapshots" and that we are all unaware of statistical mechanics and ensemble averaging."*
41

42 The statements that the Referee criticise, were already present in the initial version of the
43 manuscript. The point is that the immediate tetrahedral structure around a single water is often
44 imagined (and pictured in many articles and presentations!) as a that from the crystal. I think that
45 such representations are directly inspired by snapshot visualisations. I have altered some statements
46 in this paragraph to appear less "offending" as the Referee seems to suggest. Also, the paragraph
47 serves initially to introduce the pair correlation as a proper observable, which then leads naturally to
48 investigate the 3PS. In that sense, I think that the whole paragraph is quite coherent.
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52 *"In essence the author wants to make a rather straightforward point: that tetrahedral hydrogen-*
53 *bonding interactions and packing effects compete so that their long-range *individual* correlations*
54 *cancel each other beyond 3 molecular diameters. And furthermore this effect need not be explained*
55 *as a mixture model of a LJ liquid and ice, but instead is consistent with homegeneous fluctuations*
56 *in the bulk liquid."*
57

58
59 I am afraid I do not understand what the Referee is suggesting, at least not clearly enough to take
60 the risk of altering the manuscript subsequently. Moreover, I do say in the manuscript some of the
statements that the Referee suggests, as for example that the mixture model is not correct (in the
Conclusion for example). The effective cancellation of correlations is also many times mentioned in

1
2 the manuscript.
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4 *“Certainly the introduction could be better written to state these points. In fact the conclusion*
5 *section is more clear on these points, and maybe that discussion could be moved to the*
6 *introduction.”*
7

8
9 I thank the Referee for his positive statements on the Conclusion. I wish the Referee had exactly
10 said which points he wanted me to move to the Introduction. I personally find that the topics in the
11 Introduction are very different than in the Conclusion. There, I was setting up the scene to introduce
12 the 3PS and subsequent facts, while in the Conclusion I dwell on the consequences of the 3PS
13 finding. In the doubt, I have preferred not to alter these two parts.
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On the microscopic structure of liquid water

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August 19, 2011

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Abstract

The radial distribution function of liquid water, as obtained by the computer simulations of several classical models of water, is re-examined herein and shown to display two intriguing features. These consist in a compact “three-peaks structure” over three molecular diameters, which is followed by an apparent loss of the packing correlations beyond $R_c \approx 9\text{\AA}$. This is in contrast with simple liquids for which the correlations decay continuously with distance. This structure is reproduced for many widely used classical force fields models of water and by scattering experiments as well. It is also preserved in aqueous binary mixtures of organic solvents, even up to equimolar mixture in some cases. The analysis of the structure factor highlights the role played by the competition between packing effect and the Hydrogen bonding interactions. This analysis, in terms to competition of two length scales, is also supported by a simple core-soft model, that reproduces the structural features outlined above.

1 Introduction

Water is certainly the natural substance that has the most known anomalous properties. These properties arise ultimately from the very specificity of the pair interaction between water molecules, namely the hydrogen bond. The resulting local tetrahedral structure of liquid water has been the subject of many tentative descriptions over the past decades, among which the two-waters mixture (or iceberg) model¹⁻³ and the hydrogen bond percolation model,⁴ as well a combination of both.⁵ Although such structural models provide an intuitive picture of the cooperative extension of the local Hydrogen

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8 bonded (H-bond) tetrahedral structure,⁶ the various experimental investigations,
9 either by structural analysis^{7,8} or by various spectroscopic techniques,⁹
10 are not directly supportive of such pictures, although never clearly stated.
11 For example, it is not possible to observe two different motions of water at the
12 very short times,⁹ which would confirm that two types of water environments
13 exist. On the other hand, neutron experimental¹⁰ studies of the temperature
14 dependence of the position of the first peak of the structure factor, indicate
15 that the local environment of a single molecule goes from tetrahedral-like
16 at low temperatures to disordered at higher one. The numerous interaction
17 models of water¹¹ and their computer simulations also do not provide direct
18 conclusive evidence to support these ideas about the structure of liquid water.
19 More recently introduced water-like models, such as the Jagla model,¹²⁻¹⁴
20 for example, indicate that the corresponding liquid might coexist under two
21 different forms, although at temperatures corresponding to the supercooled
22 regime. Similar discussions on the possible underlying heterogeneous structure
23 of liquid water has been conducted even very recently.¹⁵⁻¹⁸

24
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26 The intuitive pictures that guide the ideas about the local structure of
27 a liquid are often based on an instantaneous snapshot-like visions. This
28 is particularly true for water and the ice-like tetrahedral disposition of the
29 water molecules around a single central molecule. In Statistical Mechanics
30 however, such snapshot corresponds to *one* micro-state, whereas any measure
31 of a system at equilibrium should correspond to an average over all possible
32 such micro-states. The question is then to figure out how such successive
33 averages keep or destroy the picture made out of one snapshot. Such question
34 makes no sense for an ordinary liquid that is essentially disordered, but in
35 the case of water, which is strongly ordered at molecular level through the
36 H-bond network, such question does not lead to a trivial answer. Therefore,
37 one may ask if the peculiar properties of liquid water can be seen directly on
38 *the averaged structure*, which statistical representation is the pair correlation
39 function.¹⁹ We wish here to emphasize that this correlation function is an
40 observable of the statistical description of any liquid. This function has been
41 reported many times for the case of liquid water, but only the molecular
42 structure corresponding to the first two peaks is usually discussed.^{7,8} The
43 peculiar ordering in liquid water may need a detailed investigation of what
44 happens at larger molecular separations. Such a study, conducted here for
45 several popular water models, and under various system sizes, reveals that
46 the short and long range ordering of liquid water is indeed very different
47 than that of any simple liquid. We analyse here how these findings are
48 compatible or not with previous structural models, and if newer pictures can
49 be formulated.
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2 Computer simulations and results

Herein, we focus on three popular and robust interaction models of water, namely the SPC/E,²⁰ the TIP4P²¹ and the TIP5P²² models. All these models consists of a single Lennard-Jones site with several embedded point charges corresponding to that of the oxygen and the two hydrogen atoms. Constant NPT Molecular Dynamics simulations have been conducted for the ambient conditions, temperature of 25°C and pressure of 1 atm. Berendsen thermostat and barostat were used, with relaxation times of 0.1ps and 0.5ps, respectively. The equations of motion were integrated with a time step of 2fs, which is generically used in modern simulations of water and aqueous mixtures. Earlier simulations with a time step of 0.5fs did not give appreciably different results ad far as static properties are concerned, such as in the present work. The Lennard-Jones (LJ) interactions were truncated at one third of box size and Ewald summation was used for the Coulomb interactions. Ewald summation is usually slower than reaction field techniques, but it is a rigorous account of the Coulomb long range interactions in periodic system, and does not suffer from cutoff artifacts or the need to impose the bulk dielectric constant. For the computation of the sum in the reciprocal space, 10 reciprocal space vectors in each direction were used, with a spherical cutoff for the reciprocal space sum of $n_x^2 + n_y^2 + n_z^2 < 105$. The width of the screening Gaussian was set to 0.36 Å. The values In order to probe the long range part of the pair structure, we have used a large number of particles, namely N=2048 water molecules. In order to test any possible system size dependence to the feature reported here, several system sizes were investigated, ranging from $N = 864$ to $N = 10976$ water molecules. It is important to note that the interaction and force cutoff scales with the system size since the LJ interactions are truncated at half-box length. For each system, the radial distribution function (RDF) was sampled every 50fs, between 1000 to 2000 times. These statistics ensure smooth enough RDF that can provide noiseless structure factors upon direct Fourier transformation. The generic features of the force field models, as well as the differences between them, are well known,⁸ and do not need to be repeated here.

2.1 The structure of liquid water

In order to fix the general idea about the structure of a simple disordered liquid, we report in Fig.1 the radial distribution functions $g(r)$ for a typical Lennard-Jones liquid, with a molecular diameter similar to that of water $\sigma_W = 3.165\text{Å}$ and energy parameter $\epsilon/k_B = 100K$. Two densities have been considered, one with box size is $L = 40\text{Å}$ and $N = 2048$, which corresponds

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8 the reduced number density of water $\rho^* = (N/L^3)\sigma_W^3 \approx 1$, under ambient
9 conditions, and the other corresponds to a lower density of $\rho^* = 0.73$, with
10 $L = 44.64\text{\AA}$ with the same number of particles. This latter density would
11 correspond to that evaluated for a smaller water-water “contact diameter”
12 $\sigma_{eff} \approx 2.84$, corresponding to the first peak of the experimental RDF of
13 water. The reason for considering this lower density is to follow the reasoning
14 found in the literature that water would appear as less dense because water
15 molecules could come into contact at a smaller distance -that of the hydrogen
16 bonding distance- than the actual molecular diameter σ_W . Fig.1 shows
17 that the molecular packing typical of liquid like order is seen to extends to
18 many molecular diameters, in both cases. This is particularly visible in the
19 inset, when showing the integrand $r^2h(r)$ of the isothermal compressibility¹⁹
20 $(\partial\rho/\partial\beta P)_T = \int d\vec{r}h(r)$, where $h(r) = g(r) - 1$, ρ is the number density, P
21 the pressure and $\beta = 1/k_B T$ the Boltzmann factor. The remarkable point
22 is that the *envelope* of the decay of the oscillations is a smoothly decaying
23 function of the distance.
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26 Turning now to water, the radial distribution functions between the oxy-
27 gen atoms $g_{OO}(r)$ are shown in Fig.2, for all the models investigated here.
28 There are well known differences between this RDF and that of a compar-
29 ative simple liquid:⁸ the first peak is narrower and shifted inward, because
30 of the strong directional H-bond interaction. As a result, the coordination
31 number in the first shell is about 4 instead of 12 as for an ordinary LJ liquid.
32 Here, we wish to examine the structure beyond the first two peaks. The first
33 important observation is that the oscillatory structure, which witnesses the
34 molecular packing of neighbouring shells, is distinctly seen to extend over
35 three molecular shells: this is what we call the 3-peaks structure (3PS) of
36 water. The second important point is that the oscillatory structure corre-
37 sponding to the molecular packing appears to be strongly diminished and
38 noisy beyond $r \approx 9 - 10$. In order to see this feature more clearly, we
39 show in the upper inset the same integrand as in Fig.1 $r^2(g_{OO}(r) - 1)$ for
40 the SPC/E model and $N=10976$. This magnified scale shows quite well the
41 striking diminution of structure beyond $R_c \approx 9 - 10\text{\AA}$, which is close to 3
42 molecular diameters. Since the r^2 term should amplify the oscillations due
43 to packing (as in Fig.1), their obvious absence beyond this cutoff indicates
44 that the packing correlations beyond R_c are of a different nature than those
45 for smaller distances. When compared to corresponding features of ordinary
46 liquid in Fig.1, the contrast is striking, and reveals that water has very dis-
47 tinct features extending much further than immediate neighbourhood of a
48 single molecule. Fig.3 shows that similar structural features occur also for
49 the oxygen-hydrogen (OH) and the hydrogen-hydrogen (HH) correlations. In
50 particular, the diminution of the structure, almost like a random noise be-
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behaviour of these functions seems to settle rather at $R'_c \geq 12 \text{ \AA}$, which is one molecular layer beyond that for $g_{OO}(r)$, as can be observed from the $r^2h(r)$ displays.

Fig.2 and Fig.3 are the principal result of this report. We wish to emphasize that the 3 site-site distribution functions provide indirectly a description of the angular correlations as well, since these are embedded inside these site-site functions from their statistical definition.¹⁹ So, the fact that the features reported here show up in all three site-site function indicates that orientational contributions play an important role. The details of structure shown here is a very intriguing result, and to our knowledge has never been reported before. The observation of this structure demands large N simulations. Similar studies for different models and different system sizes, ranging from N=864 to N=10976, give the same results, as shown in Fig.4. We note again that increasing the system size and truncating the interaction at half-box size remove all doubts that such features could arise from an artifact due to computational procedures. We also note that the TIPn models, while differing slightly at first and second shell, give strikingly similar results beyond these two shells. This indicates that the tetrahedral structure of all these models is more important than the small details by which these various force fields might differ. A closer look at the noisy structure beyond the 3PS reveals some remnant substructure that depends on models and simulation conditions. The TIPnP model simulations for N=2048 show this structure more pronounced than the corresponding SPC/E model simulations. However, this smaller structure depends also on the system size, and is more pronounced for smaller N=964 SPC/E system than for the N=10976 same system displayed in Fig.2. Resolving the issue of this smaller structure would require excessively accurate simulations on very large systems. The main point that we retain here is that the *envelope* of the oscillations drops abruptly after the 3PS, which is a behaviour very different from that of an ordinary liquid (Fig.1).

At this stage, a comparison with experiments is in order. This is shown in Fig.2, with scattering data from two references, Ref.⁷ and Ref.,⁸ and it reveals two things. Firstly, the 3PS is also reproduced by the two sets of experiments. Secondly, however, currently available experimental data do not extend far enough to allow a proper evidence for the strong damping of correlations beyond R_c . Those extracted from Ref.⁸ show clearly the 3-peaks structure, on all three panels, but the data does not extend beyond $r = 10 \text{ \AA}$. An additional problem concerning this last feature arises. Since the RDF is extracted from the scattering data through the obtention of the structure factor, it involves several numerical operations, and in particular a very accurate estimate of the of the region of k-vectors between the first

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8 peak and $k=0$ is required, in order to get an unambiguous long range part
9 of the RDF. Since the corresponding radial distribution functions, shown in
10 very many publications, are always shown for $r < 10\text{\AA}$, one may ask what
11 is the accuracy of the estimate beyond this range. I hope that this report
12 stimulates more accurate and detailed picture of the correlations beyond 10\AA .
13 Similar remarks equally holds for quantum simulations of water, for which
14 the small box sizes, imposed by the steep computational requirements, are
15 not large enough to see the 3PS of water, and even less the abrupt end
16 of the packing structure. We conjecture here that accurate experiments and
17 quantum simulations should equally show this peculiar structure, for physical
18 reasons that we discuss in the next section.
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21 A first interpretation of these two features could be as follows: water
22 molecules sense the packing effects only over a correlation shell of 3 molecular
23 layers. Beyond this shell the bulk liquid is sensed as if it was a ideal media
24 without packing effects whatsoever. This is very surprising, since ambient
25 water is very dense, with reduced density of $\rho^* = 1$, as can be deduced from
26 the mass density $\rho_m \approx 1\text{kg/l}$. For comparison, the triple point density of an
27 ordinary liquid is $\rho^* = 0.8$. The long range behaviour observed in Fig.1 for a
28 LJ liquid under similar conditions enforces the puzzling behaviour observed
29 for water. Since these long range correlations seems suppressed, one can infer
30 that the mean force potential in this range is zero, and therefore that the
31 particles do not interact with themselves in this range. One suspects that
32 this long range “ideality” is only apparent, and it hides canceling effects, but
33 which?
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37 2.2 A Core softened model of water

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39 In order to provide a qualitative explanation for the features observed, we
40 consider a core-softened model of water that we have studied recently.²³
41 Like many such models for water,¹²⁻¹⁴ the idea behind such models is to
42 mimic the low coordination number of water by *depleting* the usual number
43 of first neighbour of an ordinary liquid. This is usually obtained by adding
44 a soft repulsive core. In our model, this core is modeled by a Gaussian
45 interaction added to a soft sphere fluid with a repulsive $1/r^{12}$ interaction. The
46 LJ attractive interaction is intentionally removed to focus solely on entropic
47 effects of local organization. The interaction used here is
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$$50 \quad v(r) = 4\epsilon(\sigma_W/r)^{12} + \epsilon_G \exp(-\alpha_G(r - r_G)^2) \quad (1)$$

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52 with $\epsilon_G/\epsilon = 30$, $\alpha_G = 3.7/\sigma_W^2$ and $r_G = 0.85\sigma_W$. Such a model is meant to
53 mimic the two distances that are present in real water, namely the molecular
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8 diameter σ_W and the shorter hydrogen bonding distance $\approx 2.5\text{\AA}$. However,
9 in the present model, these 2 distances are inverted: the Gaussian distance
10 would correspond to the water diameter, and the inner core would be the
11 H-bonding distance. Despite this apparent caveat, this model has surprising
12 structural analogies with water. The resulting RDF is shown in Fig.5, in
13 addition to the RDF of the $1/r^{12}$ soft core alone shown in dashed line. Both
14 RDF are obtained from an NVT Monte Carlo simulation with $N=4000$ par-
15 ticles.²³ Whereas the RDF of the soft-sphere fluid shows a concentric shell
16 packing typical of simple liquid, that extends very far, the addition of the
17 depleting Gaussian interaction is seen to have two effects. Firstly, because
18 we have added a supplementary repulsion, we would expect the oscillations
19 in the correlation function to move away from the main peak instead of closer
20 to it -as it is observed here. This feature indicates that a specific structural
21 reorganisation has occurred, which seems to bring particles closer than ex-
22 pected, as a result of the competition between the dense packing and the
23 additional repulsion. Secondly, the correlations beyond $3\sigma_W$ are strongly
24 damped, which appears then to be the result of this enhanced short range
25 structure. The resulting correlation function is clearly seen to be very much
26 water-like, with the two features reported above. The diminutions of cor-
27 relations beyond $3\sigma_W$ is not as pronounced as for water. Nevertheless, it
28 is striking that an *isotropic* interaction model should capture most of the water
29 structure. The reorganization induced by the Gaussian repulsion is then to
30 enhance correlations at short range, around a shell of radii $3\sigma_W$, and the
31 damping of correlation beyond seems the result of this local constriction. It
32 therefore indicates that correlation beyond $3\sigma_W$ are damped as the result of
33 long range competing effects.

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38 This study shows that a simple two-core model is able to reproduce fea-
39 tures similar to real water, within the statistical observable of the structure,
40 namely the radial distribution function. Beyond the apparent frustrating
41 simplicity of the model, it reveals the underlying features that may help un-
42 derstand the special structure of real water, namely the presence of 2 contact
43 distances.
44

45 46 47 2.3 Influence of solutes

48 What happens to this remarkable structure when water is mixed with an or-
49 ganic solute? In Fig.6 the water-water RDF obtained from simulations RDFs
50 is shown for three binary aqueous mixtures, for low (20%) and equimolar
51 (50%) solute contents.
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53 The solutes are acetone (OPLS model²⁵), methanol (OPLS model²⁴) and
54 formamide (Cordeiro model¹⁴), which cover typical polar solutes with very
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8 different hydrogen bonding ability to water. Acetone is an H-bond acceptor
9 with a large hydrophobic group of two methyl groups, methanol is the small-
10 est alcohol and amphiphilic molecule, with both donor and acceptor abilities,
11 and formamide is a typical polar solvent with no hydrophobic groups. All
12 three solute mix with water in all proportions. Different water models are
13 used, to show the universality of the features. The TIP4P model is mixed
14 with acetone, and the SPC/E water model is mixed with the two other so-
15 lutes. The structural results depend on the choices for different models of
16 solute or water force fields, as was illustrated in Ref.,²⁶ but the main features
17 that we want to focus on herein are invariant. All simulation have been done
18 with N=2048 particles with conditions similar to the neat water. The most
19 striking feature in Fig.5 is that the 3PS of water is preserved for all these
20 three mixtures and for the different solute concentrations. There is some loss
21 of the 3PS in the case of the equimolar aqueous-formamide mixture, which
22 is presumably due to formamide molecules being able to mix well with water
23 because of the absence of hydrophobic groups and 3-fold H-bonding ability.
24 One should keep in mind that all these results involve models. However,
25 the similarities indicates a feature that should be a property of the real sys-
26 tems. The persistence of the 3 peak structure in mixtures indicates that
27 water preserves its local H-bond structure, even in presence of large amounts
28 of solutes. This seems to indicate that water molecules form coherent lo-
29 cal structure between themselves, that are robust and persistent enough to
30 survive in presence of a relatively dense solute environment.
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36 2.4 Structure factor

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38 Long range correlations are best observed in the reciprocal space, thus the
39 structure factor (SF) is a key point in the investigation. Indeed, this quantity
40 is obtained directly from various neutron or X-ray scattering experiments.
41 These can be compared with the SFs calculated from the RDF obtained
42 in our simulations. The SF is simply the Fourier transform of the RDF
43 $S(k) = \int d\vec{r} \exp(i\vec{k}\cdot\vec{r})(g(r) - 1)$.
44

45 First of all, in order to have an idea of what to expect, we show in Fig.7 the
46 SFs of the core-softened model studied above. The structural changes from
47 the SF of the soft $1/r^{12}$ interaction to the SF when the Gaussian interaction
48 is turned on, are twofold. First, the global oscillatory structure is seen to be
49 shifted outward, which confirms again that the resulting packing structure
50 is constricted, as observed in Fig.5. Second, the first peak is broadened
51 and split in two. This can be almost considered as a two-peak structure, as
52 if the main peak was shifted outwards and a smaller “pre-peak” feature had
53 emerged. However, the interpretation in favour of the pre-peak is not correct,
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8 because, as was shown in Refs,^{34,35} there is no distinct cluster structure that
9 could be associated with such a pre-peak, in contrast to what is observed
10 for alcohols. The split peak structure is then a direct consequence of a dual
11 structural correlations observed in the RDF, namely both the 3PS and the
12 loss of correlations at long range.

13
14 Returning now to the SF of water, we plot in the top panel of Fig.8 the
15 OO, OH and HH partial SFs for the SPC/E model, together with the OO
16 experimental SF, as measured by X-ray diffraction.⁸ The two compare quite
17 well and despite some minor glitches, the principal features are reproduced.
18 Other water force field models compare equally well and are not shown. The
19 most important feature is the first split-peak, which is unexpected for a single
20 component liquid.

21
22 In the following, we focus on the split peak feature. In simple liquids,
23 as shown in dashed lines in Fig.7, this main peak is positioned at a k-vector
24 $k \approx 2\pi/\sigma$, where σ is the atomic diameter.¹⁹ A pre-peak can be observed in
25 systems such as micro-emulsions,³³ which corresponds to the characteristic
26 mean size of the micelles or any other structure that can form, such as bi-
27 continuous domains or lamellae.³³ In associated liquids, such as alcohols,
28 a pre-peak can appear that corresponds to the formation of clusters.^{34,35}
29 In view of these facts, the interpretation of the split-peak of water is very
30 peculiar. The inner part of this peak is positioned at $k \approx 2\text{\AA}^{-1}$, corresponding
31 to $\sigma_w \approx 3.15\text{\AA}$, the diameter of the water molecule. The position of the taller
32 part of the main peak is at $k \approx 3\text{\AA}^{-1}$, corresponding to the OH contact
33 distance, estimated at $\sigma_{OH} \approx \sigma_w/2$ from Fig.3. It is then remarkable that
34 the inner peak is *the main structural peak*, due to molecular packing, while
35 the taller second peak (or “outer-peak”) is due to the H-bonding correlations.
36 Since both are part of the main peak of the SF, it means that packing and H-
37 bonding structural arrangement must have distinct statistical contributions,
38 and form the basic structure of the correlations *in the entire liquid*. With this
39 respect, it is quite interesting that the neutron scattering, which sees only
40 the structural distribution of neutrons in the liquid, leads to a SF with a
41 single peak,²⁷ precisely centered at the packing structure at $k \approx 2\text{\AA}^{-1}$, while
42 the X-ray scattering, which sees the electronic structure, is able to report the
43 splitting of the peak due to the H-bonding structure at a larger k-vector.

44
45 Following the analysis in amorphous ice,³² these structural features can be
46 further clarified by analyzing the underlying Bathia-Thornton SFs,²⁸ which
47 would correspond to the density-density (NN) and charge-charge (CC) cor-
48 relations, as if water was an atomic mixture of oxygen and hydrogen atoms.
49 These structure factors are defined as²⁸

$$S_{NN}(k) = x_O^2 S_{OO}(k) + x_H^2 S_{HH}(k) + 2x_O x_H S_{OH}(k) \quad (2)$$

$$S_{CC}(k) = x_O x_H [S_{OO}(k) + S(k) - 2S_{OH}(k)] \quad (3)$$

$$S_{NC}(k) = x_O x_H [x_H (S_{HH}(k) - S_{OH}(k)) - x_O (S_{OO}(k) - S_{OH}(k))] \quad (4)$$

in terms of the previous SFs and the mole fractions of the oxygen and hydrogen atoms, $x_O = 1/3$ and $x_H = 2/3$, respectively. Note that in the original definition the CC structure factor stands for concentration-concentration and measures the fluctuations in the repartition of the two species, which are here H and O, hence the renaming into charge-charge. These new SFs are represented at the lower panel of Fig.8. They are nearly structureless since the molecules are rigid, hence there is no fluctuation in the atomic positions. However, it is clearly seen that the split-peak structure has been now distributed between S_{NN} and S_{CC} . The main peak of the density-density SF $S_{NN}(k)$ is exactly at the pre-peak corresponding to the packing structure $k \approx 2\text{\AA}^{-1}$, while the charge-charge peak for $S_{CC}(k)$ is positioned exactly at $k \approx 3\text{\AA}^{-1}$.

These facts confirm that the features of the split peak are governed by the dual competition effects of packing and H-bond correlation effects. The apparent loss of packing correlations seen at long range is therefore the result of a compensation effect to enhanced H-bond OH correlations. The simple isotropic model confirms that this effect is more of an entropic origin -due to local reorganizations - than energetical, in the sense of H-bond energetics. Thus water is very strongly ordered at all scales.

3 Outlook and conclusion

The picture that finally emerges from all these results, is that water-water correlations are dominated by H-bonding and packing correlations that appear to *cooperate constructively* at short distance, within a radius of $R_c \approx 3\sigma_W$, and to *cooperate destructively* beyond, giving rise to the strong diminution of the correlations observed in all models. In view of the high packing density of water, this observation seems to suggest that the H-bonding correlations must be very important beyond R_c , since they nearly obliterate the natural packing correlations that should exist in this region, just like for the LJ liquid in Fig.1. Therefore, the apparent absence of correlations seems to hide some “mixture” of correlations that extend quite far in the bulk. At the same time, however, we do not see any sign that such correlations are accompanied by long range density correlations, as in a liquid close to the spinodal for example. These correlations appear therefore as structural -as part of a special local structure, and not induced by density fluctuation. With that respect, small angle X-ray scattering has revealed²⁹ weak enhancement of the

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8 structure factor at $k=0$, even at room temperature quite far from any
9 critical phase transition, which may provide some indirect support for special
10 type of correlations that are not critical fluctuations as such.^{17,18} The field
11 theoretic approach formulated by Tanaka,³⁰ based on the idea of the compe-
12 tition of a density field and an H-bond ordering field, offers some support to
13 the BT analysis of the structure factor.
14

15 In this study, we have examined models without polarisation. One
16 may ask if polarisation effects would alter the picture of the 3PS. Since the
17 origin of the 3PS is the existence of 2 cores, that of the molecular diameter
18 and the Hbonding distance, it is hard to see how polarisation effects can
19 suppress this duality. They would rather change slightly their magnitude.
20 In other words, we expects that more realistic force field models of water
21 will reproduce the 3PS. One way to check this conjecture would be to obtain
22 accurate scattering data for the correlations beyond the 10Å range in which
23 they actually appear to be confined.
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25 From methodological point of view, the analysis of the structure of wa-
26 ter based on a statistically and computationally accessible quantity, namely
27 the pair density correlation function, is probably more precise than consid-
28 erations based on the analysis of thermodynamical quantities. As stated in
29 the Introduction, it is a statistical observable of both experimental and com-
30 putational studies. The result of the analysis provided here is not directly
31 supportive of the two models mentioned in the Introduction, the iceberg
32 model or percolated liquid model. The fact that our previous direct cluster
33 analysis of water did not reveal the existence of distinct aggregates, such
34 as those which were found in simple alcohols,^{34,35} is a strong evidence that
35 water is not to be looked as a mixture of a two local structures. Rather,
36 the presence of two correlations scales separated by R_c , naturally suggests
37 the picture for liquid water based on correlations, rather than that of clus-
38 ters based on an instantaneous snapshot vision. In this picture, water is a
39 molecular liquid which has very specific correlations, that I would call “cor-
40 relons”, each of size $2R_c$, which would correspond to the 3PS. Such entities
41 are not necessarily tetrahedrally ordered, as in an instantaneous view would
42 naively suggest, but averages of local order that appear at the density cor-
43 relation level. Such entities would be ideal between them, or only weakly
44 interact between themselves, which would then explain the strong damping
45 of correlations beyond R_c . As such, they would freely overlap, which means
46 that there is no particular center for such a correlon, as opposed to a spe-
47 cific cluster. This would explain why specific clusters were never observed,
48 or why there is no strong evidence for a 2-water structure as it is usually
49 pictured. Peculiar clustering features have been reported by some authors
50 lately, in cold water³⁷ as well in supercooled water,³⁶ and these could have
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8 a relation with the 3PS reported here. In any case, the analysis shows that
9 water in ambient conditions, despite being a disordered liquid, hides consid-
10 erable amount of order that extends quite far from a single molecule, and
11 which make it an unusual liquid.
12

13 14 15 Acknowledgments

16
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19 enlightening discussions.
20

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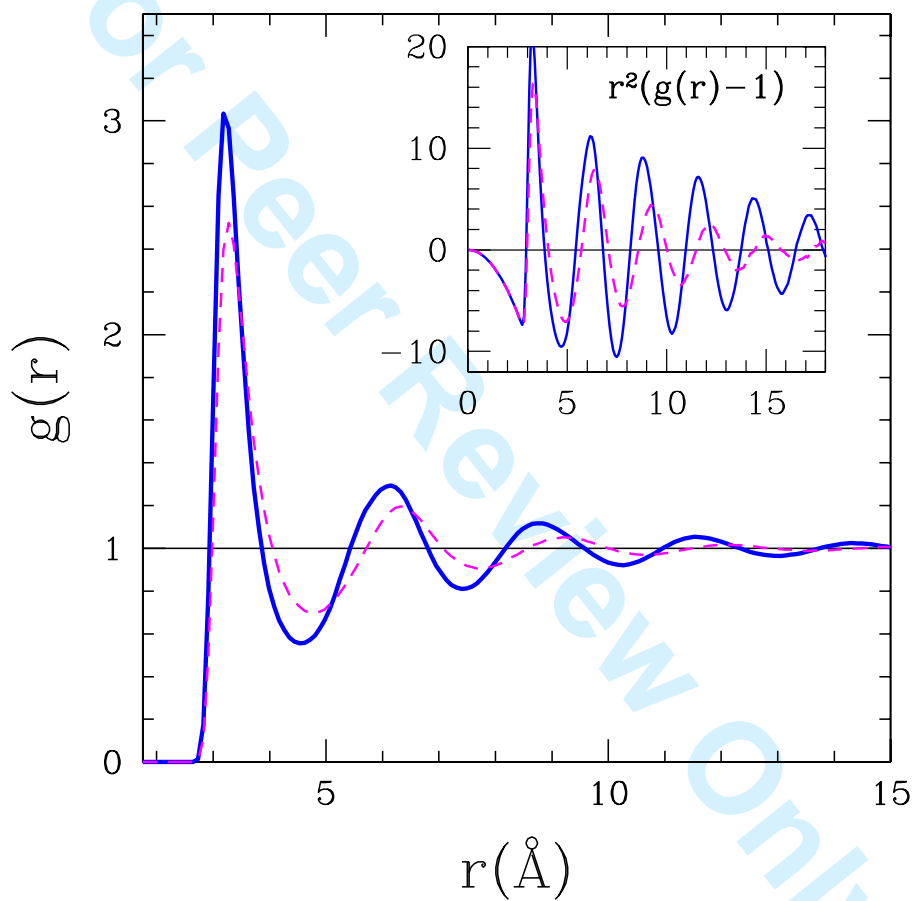
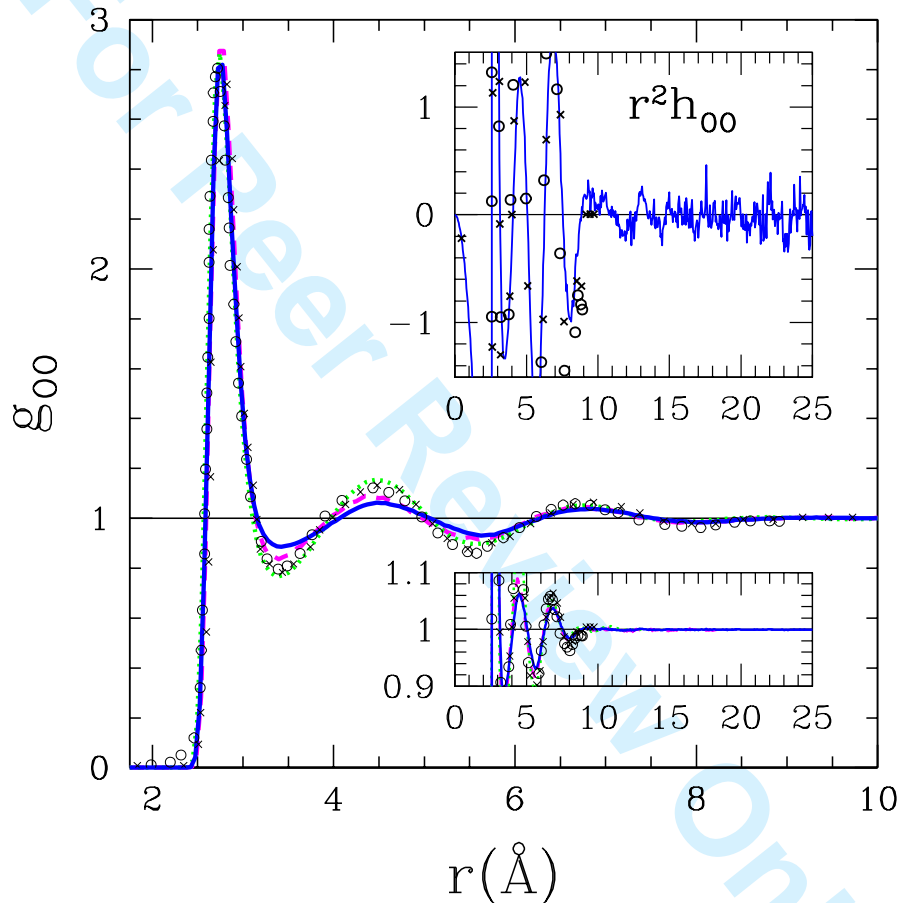
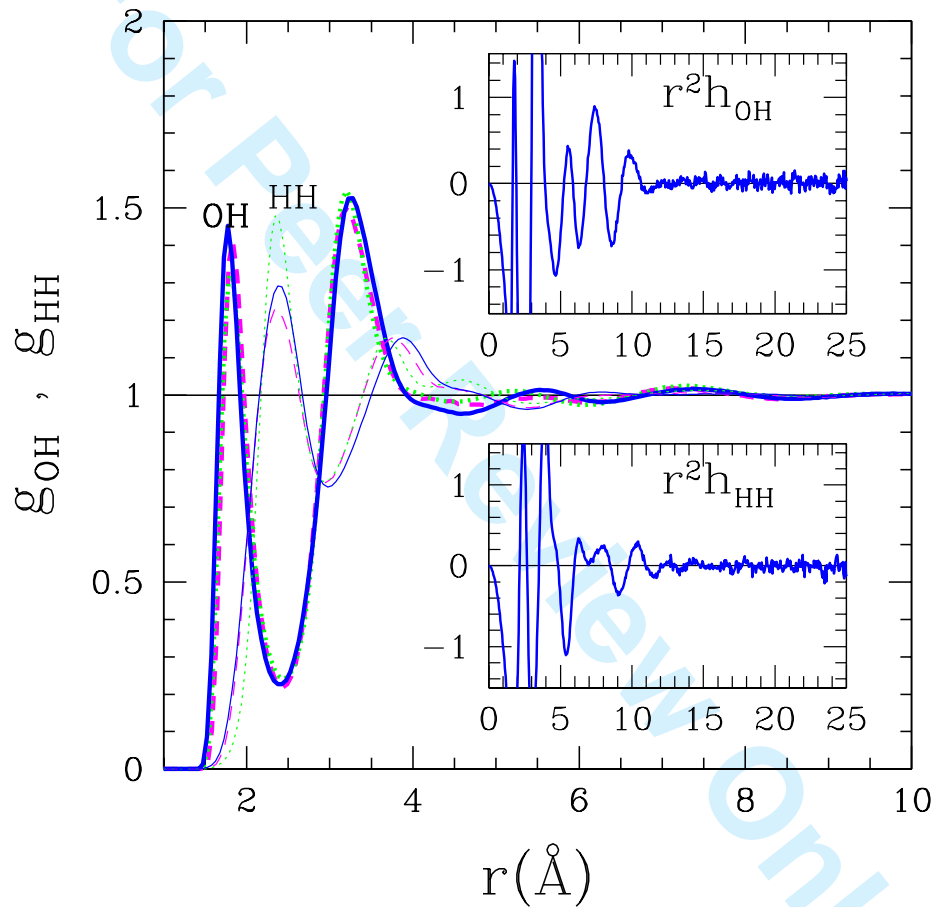


Figure 1: Typical liquid state radial distribution function for reduced densities $\rho^* \approx 1$ (full line) and $\rho^* = 0.73$ (dotted). The inset shows the integrand (note the difference in vertical scale in the inset)



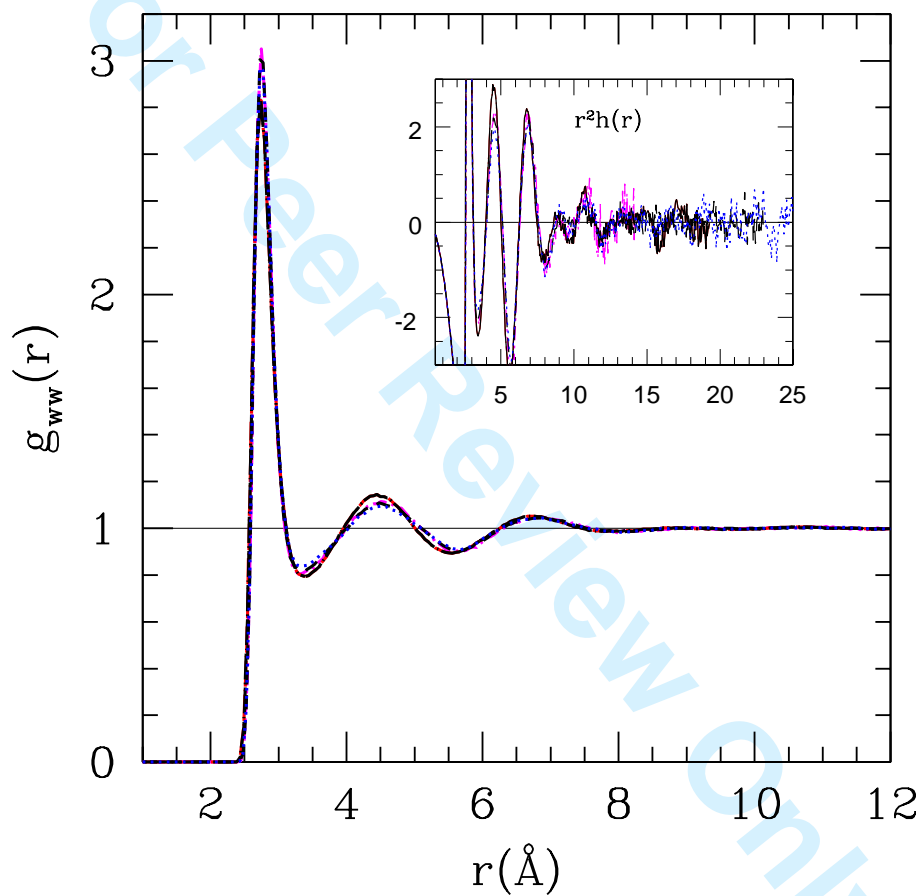
Perera Fig.2

Figure 2: The oxygen-oxygen (OO) RDF for the three water models: SPC/E(full line) , TIP4P(dashed) and TIP5P(dotted) , experimental data from Ref⁷ crosses and Ref⁸ (open dots). The lower inset is a close up of the long range correlations. The upper inset shows the integrand of the compressibility (see text) for the SPC/E mode



Perera Fig.3

Figure 3: The oxygen-hydrogen and hydrogen-hydrogen radial distribution functions for the three water models: same line code as in Fig.1. The upper inset is a close up of the OH integrand and the lower inset for the HH correlations, both for the SPC/E model



Perera Fig.4

Figure 4: Test of the model and size dependence of the features: full line TIP5P(N=2048), dash-dotted TIP4P(N=2048), dashed SPC/E(N=864), big dashes SPC/E=4000),dotted SPC/E(N=10976).

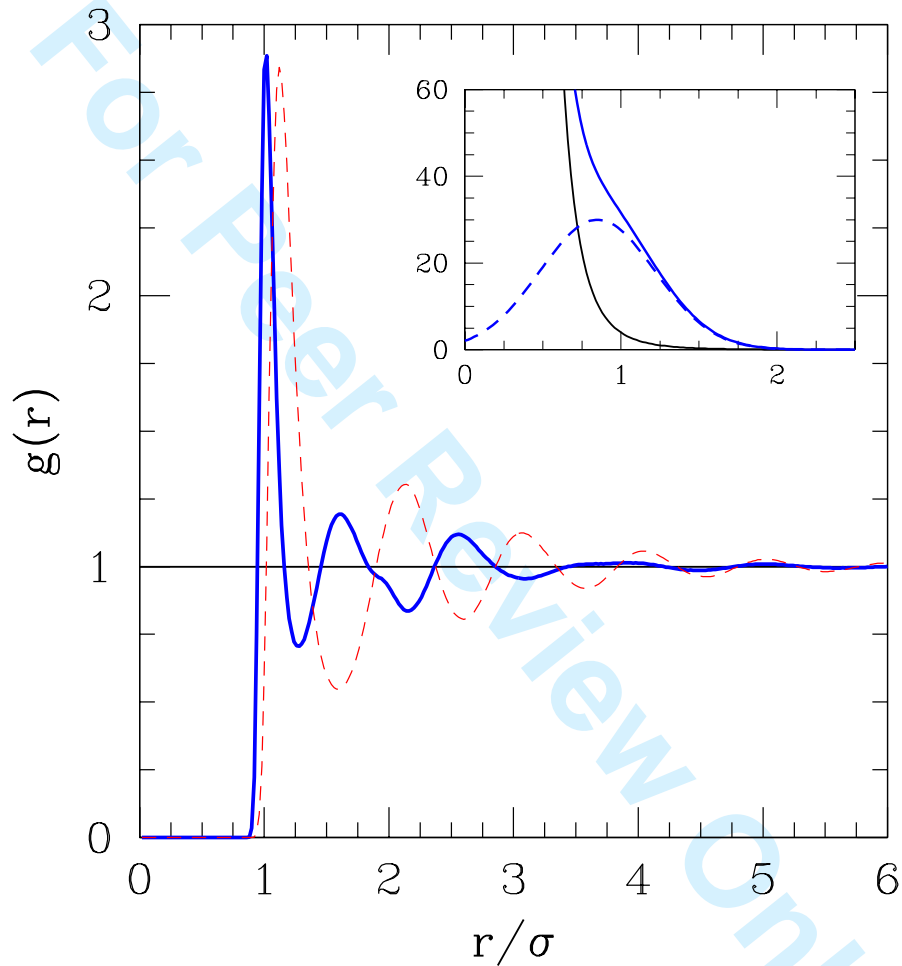
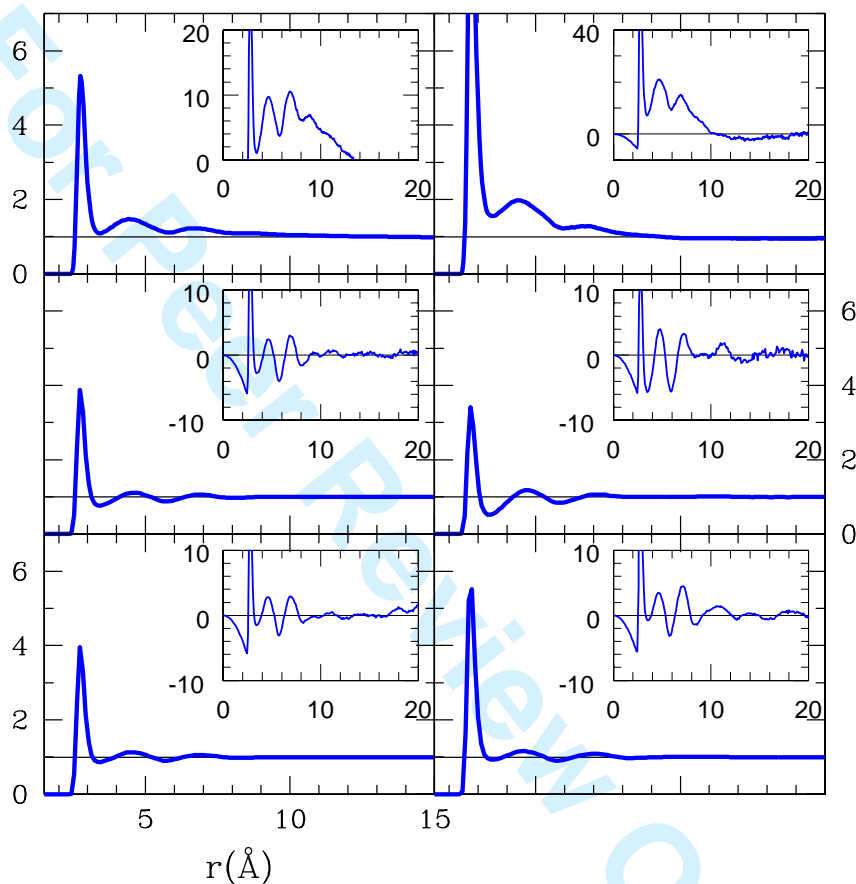


Fig.5 Perera

Figure 5: The RDF for the core-softened interaction. Full lines MC simulation results. The dashed curve is the MC RDF for soft repulsion alone. Inset shows the interaction: thinner full line $1/r^{12}$, dashes for the Gaussian repulsion and thicker full line for core-softened interaction.



Perera Fig.6

Figure 6: Behaviour of the “3-peaks structure” of the water-water RDFs, for three different binary aqueous mixtures, with three different organic solvents: acetone (the two upper panels), methanol (middle panels) and formamide (lower panels). Left panel is 20% organic solvent content and right panel for 50% content. The insets show the integrands. The vertical and horizontal scales are kept the same in all 6 main panels.

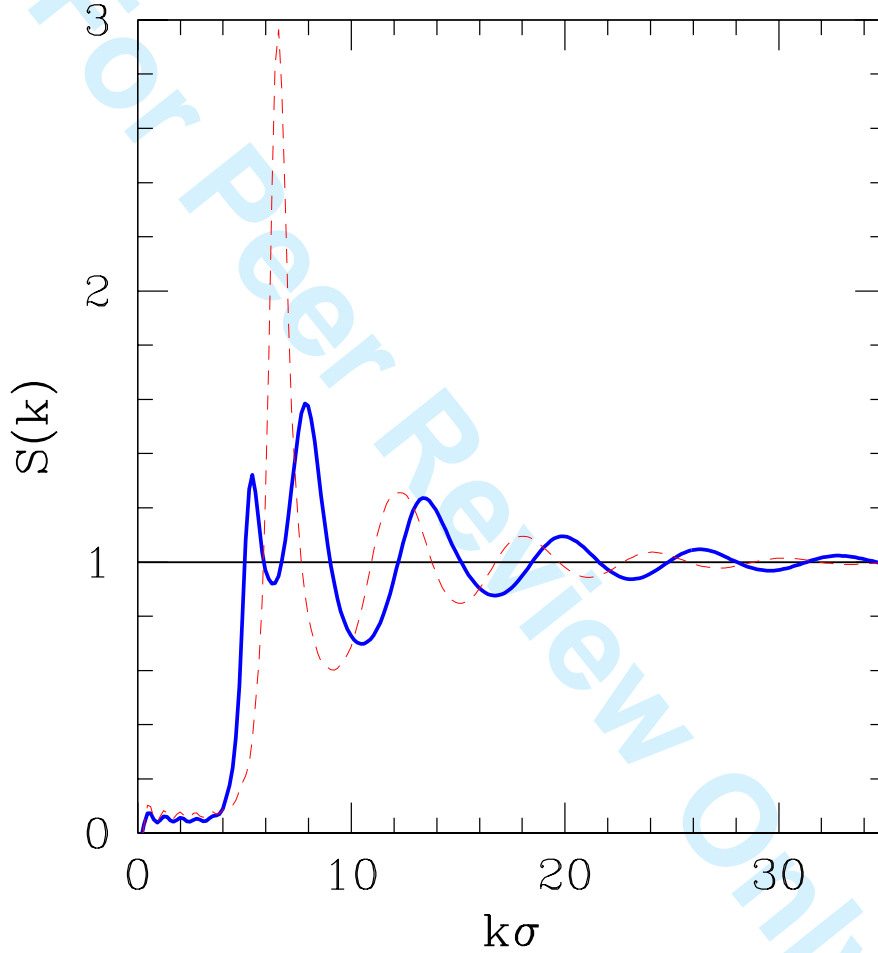


Fig.7 Perera

Figure 7: Structure factors corresponding to the RDFs of the core-softened model in Fig.5, with same line conventions

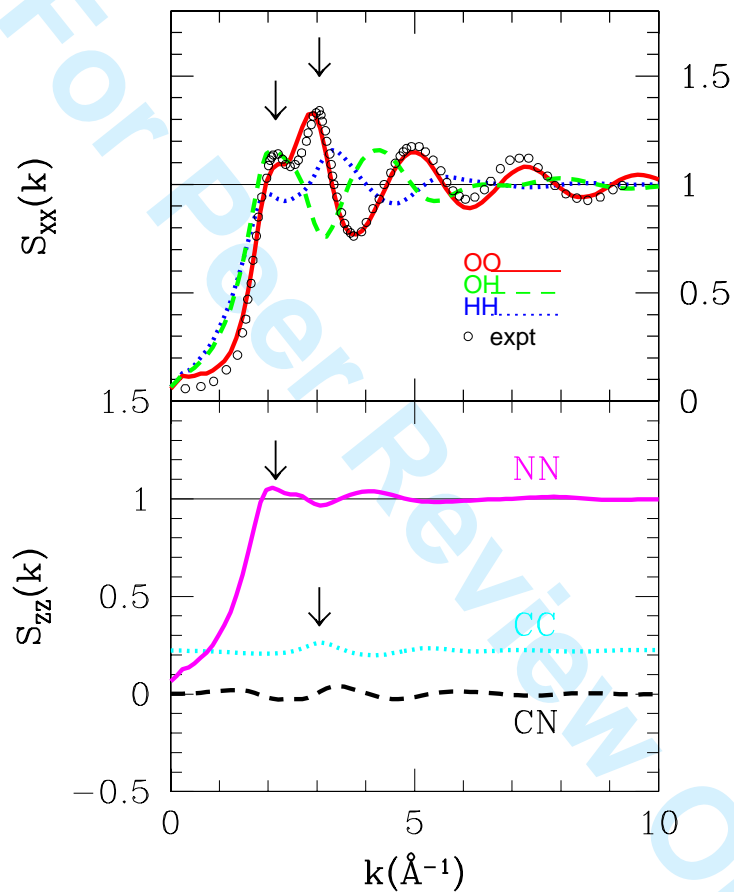


Fig.8 Perera

Figure 8: Top panel: the three site-site SFs for the SPC/E water model(OO (full line), OH(dashed) and HH(dotted)), with the experimental SF from Ref⁸ (open dots). The arrows point at the two split-peaks. Bottom panel: the Bhatia-Thornton SFs discussed in the text. The arrows point at the same peak positions as in the upper panel.