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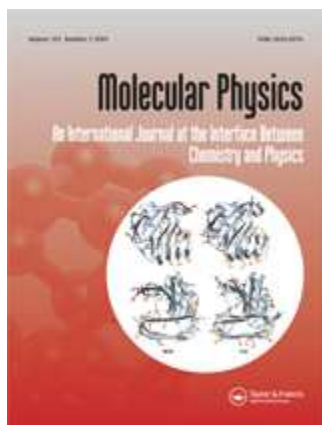
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Structural transformations in amorphous ice and supercooled water and their relevance to the phase diagram of water

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(Dated: March 17, 2008)

Arguably the most important liquid in our existence, water continues to attract enormous efforts to understand its underlying structure, dynamics and thermodynamics. These properties become increasingly complex and controversial as we progress into and below the “no man’s land” where bulk water can only exist as crystalline ice. Various, so far unconfirmed, scenarios are painted for this region, including the second critical point scenario, the singularity-free scenario, and most recently the “critical point-free” scenario [C.A. Angell, *Science*, **319**, 582 (2008)]. In this article the structural aspects of water (as opposed to its dynamic and thermodynamic properties) in its supercooled, amorphous and confined states are explored, to the extent that these are known and related to the water phase diagram. An important issue to emerge is the extent to which structural measurements on a disordered material can tell us about its phase.

I. INTRODUCTION

Figure 1 shows a simplified phase diagram of water in the ambient and low temperature region. In particular it is seen that, starting from ambient pressure, the melting point falls to about 251K at a pressure of 0.2GPa, then rises to higher temperatures with further increases in pressure. Below the equilibrium melting line lies the homogeneous nucleation line - this is the lowest temperature to which the liquid can be cooled before spontaneous crystallisation sets in: the bulk liquid cannot exist below this line. At ambient pressure it occurs at 231K. At much lower temperatures, below 150K, water can be made to form an amorphous solid, either by condensing water vapour onto a cold substrate, or by hyperquenching droplets of the liquid, or by pressurising crystalline ice to around 1GPa. The material made by the latter process is actually a high density form of amorphous ice, called HDA: when the pressure is released it converts spontaneously to the low density form, LDA, which, structurally at least, appears very similar to the amorphous ices formed by vapour deposition and hyperquenching. Subsequently an even denser form of amorphous ice was found, VHDA, formed by annealing HDA under pressure at 120K. When the pressure is released VHDA converts directly to LDA and does not stop at HDA on the way, so there is a debate about whether VHDA is truly a new form of amorphous ice, or whether it is simply densified, annealed HDA. The space (shaded in Fig. 1) between the highest amorphous ice formation temperature, T_X , and the homogeneous nucleation line, T_H , is often called “no man’s land” since experiments on the bulk liquid in that region are impossible.

Comprehensive and very readable reviews of the current state of thinking on supercooled water were published in 2003.[1, 2] At that time there appeared to be two

competing scenarios for understanding the properties of supercooled and glassy water. One of these was the proposal that at a temperature of around 220K and pressure of 0.1GPa, water exhibited a second critical point below which it separated into one of two distinct forms, high density liquid (HDL) and low density liquid (LDL), with a first order transformation between them. These liquids were a continuous extension of their much lower temperature amorphous counterparts, HDA and LDA respectively. The increase in density and entropy fluctuations as one approached this critical point could be used explain the increased compressibility and heat capacity of water on cooling water below its stable melting temperature. The consequences of such a second critical point would extend up into the accessible supercooled and low temperature stable liquid regions. Hence there is for example a marked but continuous structural transformation between HDL and LDL in the low temperature stable liquid region [3]. However the difficulty of observing this second critical point in the bulk liquid, or even getting close to it, means it is ‘virtual’ in the same sense that the focal point of a concave lens is virtual, namely you might be able to see the effects of the postulated second critical point in the stable liquid region, even though you can’t observe it directly.

This means its existence will remain controversial, since there is also the “singularity free” scenario, which reports a similar phase diagram to that with the second critical point, but without any divergences in thermodynamic quantities and with a rapid but continuous transformation between HDL and LDL. Within this scenario the transition from HDA to LDA would also be rapid but continuous.

More recently, Angell [4, 5] has proposed, in analogy to what happens in crystalline C_{60} , the hypothesis of an order-disorder transition occurring as deeply cooled water is heated, this transition occurring also at 225K. Such a transition is apparently observed in highly confined water, where the freezing transition is suppressed. It does not exclude the second critical point scenario, but it also

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1 does not require it. How this most recent suggestion re-
2 lates to the full phase diagram of cold water remains to
3 be determined.

4 It is interesting that in 1997 Jeffery and Austin, [10],
5 published an equation of state that they claimed was sig-
6 nificantly more accurate than existing equations of state
7 for water. Extrapolating this phase diagram into the su-
8 percooled region, they refer to a second critical point for
9 water and the likelihood of a high density to low density
10 transition which occurs immediately before freezing at
11 high enough pressures. These ideas were elaborated in
12 a subsequent paper, [12]. In the meantime Mishima and
13 Stanley in 1998 observed a discontinuity in the decom-
14 pression induced melting line of ice IV and concluded this
15 could mean there was a second critical point at about the
16 same pressure and temperature as Jeffery and Austin,
17 namely 0.1GPa and 220K, [11]. They do not refer to
18 the Jeffery and Austin equation of state, but the latter
19 appears to derive from previous work, [13], so it is not
20 clear how truly independent are the two results. Even so
21 it seems curious that a very accurate equation of state
22 seems to predict the same behaviour as the observed
23 ice IV melting curve. Moreover, this same equation of
24 state apparently predicts the observed low temperature
25 anomaly in the specific heat of water quite accurately, the
26 same anomaly that is used by Angell to infer an order-
27 disorder transition, [4].

28 Why is all this important and why has so much en-
29 ergy been devoted to understanding it? Well much of
30 the water that impacts most on us, such as occurs in liv-
31 ing organisms and in geological situations is not in the
32 bulk form. On the contrary this water is usually highly
33 confined to small pockets or pores and surrounded by a
34 variety of molecules such as organic peptide chains and
35 inorganic substrates (silica being a very common one). In
36 the case of the Jeffery and Austin work cited above, the
37 nucleation rate of highly supercooled micron-sized water
38 droplets is of crucial importance in atmospheric research.
39 Confined water is special because the main effect of con-
40 finement, if the confining region is small enough, is to
41 suppress crystallisation, so that the no man's land of bulk
42 water may in fact be accessible for confined water. If we
43 can find out how water behaves in no man's land, perhaps
44 we will have a better understanding of the fundamental
45 driving mechanisms for water outside of this region. In
46 fact the study of water in confinement has become a ma-
47 jor issue in its own right in recent years, and, as with the
48 bulk liquid, highly controversial, as will become apparent
49 below. Of course the truth of the matter is that much
50 of the focus on water is driven by sheer curiosity. What
51 is this material that we encounter so often? How does it
52 work?

53 It has to be said from the outset that the investiga-
54 tion of water, like presumably many other scientific "hot"
55 topics, is surrounded in controversy and disputes about
56 interpretation and data. Therefore while some common
57 factors emerge, there are still a number of outstanding
58 questions to be resolved. Even the structure of ambient

bulk water, which had generally been more or less under-
stood for many years as a tetrahedrally coordinated net-
work, was thrown into disarray in 2004 [14] with the chal-
lenging, and so far unconfirmed, proposition that water in
fact was more chain-like than network-like. Independent
evidence in support of this idea is still lacking, and the
interpretation of the x-ray absorption spectroscopy data
that led to the original proposal is controversial and not
fully understood. Nonetheless the proposal has led to a
substantial amount of research trying to corroborate or
understand the findings.

In this situation it is not possible in a review of this
kind to cover all the topics related to water with any de-
gree of completeness. Instead the aim is to summarise as
best as possible the primary *structural* aspects of ambient
and supercooled water and amorphous ice, to the extent
that these are understood, and to identify discrepancies
between different accounts. Reference to computer sim-
ulations of water will only be made where relevant, since
the computer simulation of water is itself a vast topic
that could not possibly be given adequate coverage here.
Although computer simulations of water and other mate-
rials are often labelled as being a study of that particular
material, it should not be forgotten that a computer sim-
ulation is *only* a model of the system under investigation,
and without experimental data to back it up, that model
is largely meaningless, unless, as sometimes happens, the
model is being used to test theories. An important issue
that does need to be addressed at the present time is how
to determine the structure of a disordered material such
as water experimentally: given that experiments provide
only part of the information needed to construct an ac-
curate atomistic model of the liquid, what additional in-
formation is required and where do we get it from?

In the article that follows firstly the primary methods
of getting atom-scale information on the structure of a
disordered material, namely diffraction techniques, are
described, together with a brief mention of some spec-
troscopic approaches that could be used. Then the avail-
able structures of ambient, supercooled, amorphous and
confined water are assessed. Included in this are some
comments on the ability of structure measurements to
distinguish between different phases of water. Finally
the structural information presented in the previous sec-
tions is brought together in terms of the known phase
diagram of water at ambient conditions and below.

II. DIFFRACTION TECHNIQUES AS A PROBE OF STRUCTURE

The majority of diffraction experiments on water and
amorphous ice have used either x-ray diffraction or neu-
tron diffraction techniques. The scattered radiation am-
plitude from an array of N point atoms at positions
 $\mathbf{r}_1 \cdots \mathbf{r}_N$ is given by $A(\mathbf{Q}) = \sum_{j=1}^N b_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j)$. Neu-
trons are scattered by the atomic nucleus, which is typi-
cally 10^{-4} times smaller than the wavelength of the neu-

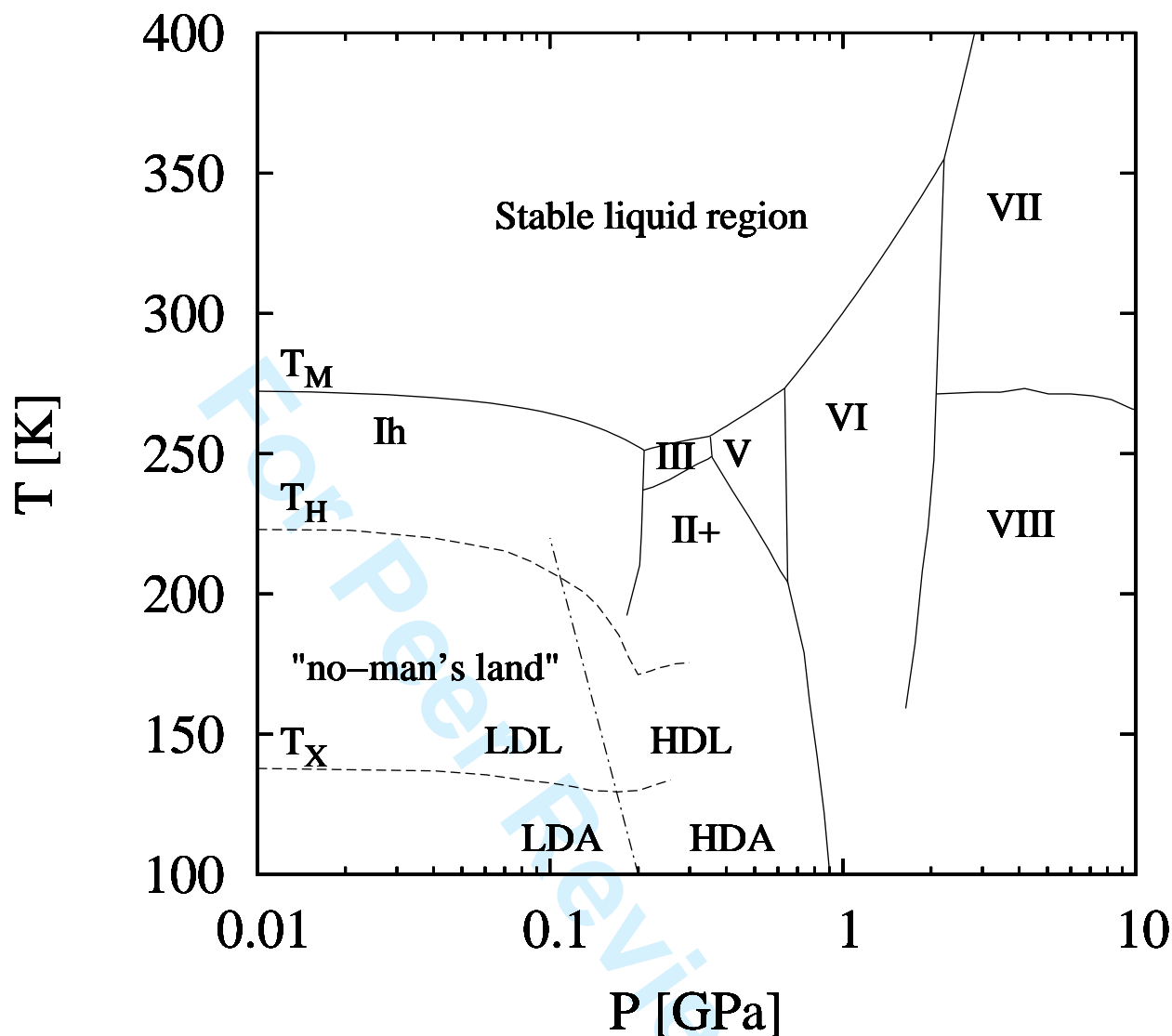


FIG. 1: The temperature-pressure phase diagram of water showing the melting line, T_M (solid), the homogeneous nucleation line, T_H (dashed), and the crystallisation line, T_X (dashed), which represents the highest temperature that amorphous ice can exist without crystallisation. The region between T_X and T_H is called "no-man's land". The liquid-ice melting lines are taken from [6]. The homogeneous nucleation line is taken from [7]. The crystallisation line of amorphous ice is taken from [8]. The transformation lines between the different ices are sketched in approximately for completeness. The region labelled ice II+ contains more than one form of ice. Also shown is the conjectured line of LDL - HDL (or LDA - HDA) transitions based on the available data, [9–11] (dot-dashed line).

tron, so that for neutrons b_j , the scattering amplitude of atom j , is simply a number independent of Q , but is characteristic of the isotope and spin states of that nucleus. Therefore the neutron scattered intensity will be averaged over the spin and isotope states of the constituent nuclei. It is in general true that these spin and isotope states do not correlate with the atomic positions, except in certain special cases such as molecular hydrogen or where isotope substitution has occurred on specific sites within a molecule. X-rays on the other hand are scattered by the atomic electrons, and so sample the electron dis-

tribution as well as the atom distribution. This electron distribution characterised by the "electron form factor", $f_j(Q)$. It is widely assumed there is no isotope or spin dependence of these form factors.

The scattered intensity per unit atom, otherwise called the differential scattering cross section, is given by:

$$\begin{aligned} \frac{d\sigma}{d\Omega}(\lambda, 2\theta) &= \frac{1}{N} |A(\mathbf{Q})|^2 \\ &= \frac{1}{N} \sum_{jk} b_j b_k \exp[i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)] \quad (1) \end{aligned}$$

Here \mathbf{Q} represents the change in wave vector between incident (\mathbf{k}_i) and scattered (\mathbf{k}_f) radiation beams. Thus $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ and the modulus $|\mathbf{Q}| = Q = 4\pi \frac{\sin \theta}{\lambda}$ where 2θ is the scattering angle and λ is the radiation wavelength.

Note that the sum in (1) can be divided into two parts, namely terms for which $j = k$, the so-called ‘self’ terms, and terms for which $j \neq k$, the ‘distinct’ or ‘interference’ terms. The self terms represent the baseline scattering that would occur in the absence of any atom correlations, while the distinct terms contain the structural information pertaining to the material under investigation.

In the limit of large N , the discrete sums in (1) become continuous integrals over the radial distribution functions of the system in question. For neutrons we obtain:

$$\begin{aligned} \frac{d\sigma^{(n)}}{d\Omega}(\lambda, 2\theta) &= \sum_{\alpha} c_{\alpha} \langle b_{\alpha}^2 \rangle \\ &+ \sum_{\alpha, \beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} \langle b_{\alpha} \rangle \langle b_{\beta} \rangle H_{\alpha\beta}(\mathbf{Q}) \end{aligned} \quad (2)$$

and for X-rays:

$$\begin{aligned} \frac{d\sigma^{(x)}}{d\Omega}(\lambda, 2\theta) &= \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) \\ &+ \sum_{\alpha, \beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q) H_{\alpha\beta}(\mathbf{Q}) \end{aligned} \quad (3)$$

where the site-site partial structure factors are

$$\begin{aligned} H_{\alpha\beta}(\mathbf{Q}) &= \rho \int h_{\alpha\beta}(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \\ &= 4\pi\rho \int_0^{\infty} r^2 h_{\alpha\beta}(r) \frac{\sin Qr}{Qr} dr \end{aligned} \quad (4)$$

and where c_{α} is the atomic fraction of component α , $h_{\alpha\beta}(r) \equiv (g_{\alpha\beta}(r) - 1)$ is the so-called ‘total’ site-site radial distribution function between atom types α and β , and $g_{\alpha\beta}(r)$ is the corresponding site-site radial distribution function. It is assumed the system is isotropic, so that $h_{\alpha\beta}(\mathbf{r})$ does not depend on the direction of \mathbf{r} .

It can be seen that for both neutrons and x-rays the scattering cross section splits into self and distinct terms as described previously. The angle brackets in (2) are the spin and isotope averages required for neutron scattering, and note how these averages are performed differently for the self terms compared to the distinct terms. For example light hydrogen in particular has two large but opposite spin dependent scattering lengths. As a result in most cases neutron scattering from light hydrogen produces a large scattering level from the self scattering, but a much weaker scattering from the useful interference scattering. Hence neutron experiments which use light hydrogen are plagued by a large background from this self scattering.

For x-rays it is customary to perform a further normalisation of the data to the product of electron form factors - this is to remove the strong Q dependence of the scattering pattern. This produces an effective interference

atomic structure factor for the material, $F^{(x)}(Q)$. Traditionally the normalisation used is $[\sum_{\alpha} c_{\alpha} f_{\alpha}(Q)]^2$, giving

$$F^{(x)}(Q) = \left(\frac{d\sigma^{(x)}}{d\Omega}(\lambda, 2\theta) - \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) \right) / \left[\sum_{\alpha} c_{\alpha} f_{\alpha}(Q) \right]^2 \quad (5)$$

but it is argued [15] that since the interference scattering oscillates around the self scattering, which acts as its baseline in the absence of atomic correlations, the correct normalisation to use for x-rays is $\sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q)$, so that

$$F^{(x)}(Q) = \left(\frac{d\sigma^{(x)}}{d\Omega}(\lambda, 2\theta) - \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) \right) / \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) \quad (6)$$

With this latter definition the positivity of $\frac{d\sigma^{(x)}}{d\Omega}(\lambda, 2\theta)$ requires that $F^{(x)}(Q) \geq -1$ for all Q , a requirement which is not necessarily met by (5). Alternatively, some authorities normalise their x-ray diffraction data to the single molecule scattering [16, 17] to leave the molecular centres distribution function. However to be valid this normalisation requires the assumption that orientational correlations between adjacent molecules do not affect the x-ray pattern measurably, an assumption which is only approximate for water.

For neutrons a variety of normalisations are in place [18]. Since the neutron scattering lengths are independent of Q it is not necessary to remove the Q dependence of the form factors as is done for x-rays. For most cases it is sufficient to define a neutron interference differential cross section as

$$\begin{aligned} F^{(n)}(Q) &= \frac{d\sigma^{(n)}}{d\Omega}(\lambda, 2\theta) - \sum_{\alpha} c_{\alpha} \langle b_{\alpha}^2 \rangle \\ &= \sum_{\alpha, \beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} \langle b_{\alpha} \rangle \langle b_{\beta} \rangle H_{\alpha\beta}(Q) \end{aligned} \quad (7)$$

which can be used for further analysis. Note that the positivity requirement on the differential cross section is independent of the values of the scattering lengths, so there is the formal requirement, as for x-rays, that

$$F^{(n)}(Q) \geq - \sum_{\alpha} c_{\alpha} \langle b_{\alpha}^2 \rangle \quad (8)$$

It should be born in mind that the form (1) contains a hidden approximation, sometimes misleadingly called the ‘static’ approximation [19, 20]. The point is that in real experiments, the radiation will either lose energy to the scattering system or gain energy from the scattering system. This is called inelastic scattering. The approximation made is that the change in energy of the incident radiation in scattering from the sample is (very) small compared to its incident energy. This approximation has been discussed extensively for both x-rays and

neutrons, but to date there are no guaranteed methods of removing the effects of inelasticity from diffraction data, except in the case of neutron scattering when the mass of the atom is much larger than the mass of the neutron [19]. For the present purposes we assume the measured data have been corrected for inelastic scattering, which affects both neutron and x-ray scattering data alike, so that the static approximation holds. However the presence of inelastic scattering in the real experiment invariably means that diffraction data may contain systematic effects which cannot be removed completely. Note also that the static approximation is *not* the same as assuming the scattering is elastic, which is what happens in the Bragg diffraction peaks from a crystal. In general it is believed [19] the inelastic scattering affects the self scattering more markedly than the distinct scattering, so that at worst it contributes an unphysical background to the diffraction data, rather than a Q -dependent factor which would be more problematic.

Water will have three site-site radial distribution functions, namely OO, OH and HH. Writing

$$w_{\alpha\beta}^{(n)} = (2 - \delta_{\alpha\beta})c_{\alpha}c_{\beta} \langle b_{\alpha} \rangle \langle b_{\beta} \rangle \quad (9)$$

and

$$w_{\alpha\beta}^{(x)}(Q) = \frac{(2 - \delta_{\alpha\beta})c_{\alpha}c_{\beta}f_{\alpha}(Q)f_{\beta}(Q)}{\sum_{\alpha} c_{\alpha}f_{\alpha}^2(Q)} \quad (10)$$

Table I lists the weights outside each of the site-site terms for x-rays and for neutrons. Note that for X-rays the diffraction pattern is dominated by the OO term, while for neutrons it is dominated by the OH and HH terms for both heavy and light water. However the OH term makes a significant contribution to the x-ray diffraction pattern, and the OO term cannot be ignored in the neutron diffraction patterns. Therefore the two types of radiation produce highly complementary structural information, and one would think, on the assumption that heavy and light water have the same structure, it would be trivial to measure the water diffraction pattern with x-rays and neutrons and produce a comprehensive view of the structure.

Unfortunately, even within this assumption, real life is not so straightforward. For x-rays it is not clear what are the correct form factors to use for water, as alluded to in Table I. Moreover the x-ray form factors diminish rapidly at high Q so that interference scattering intensities are small in this region of the diffraction pattern. At the same time the Compton scattering from inelastic x-ray scattering rises at high Q , creating a Q -dependent background that has to be estimated and subtracted. This background depends sensitively on the detector efficiency as a function of x-ray energy and the extent to which energy analysis is performed on the scattered x-rays. Hence it is never possible to subtract this background perfectly.

For neutrons an analogous problem occurs. Here the scattered intensity does not fall off at high Q as for x-rays but inelastic scattering for light atoms like H and

TABLE I: Neutron, $w_{\alpha\beta}^{(n)}$, and X-ray, $w_{\alpha\beta}^{(x)}(0)$, weightings outside the three site-site partial structure factors for water in equations (2) and (3). HDO corresponds to a 50:50 mixture of D₂O and H₂O. The modified x-ray weightings correspond to the case where modified form factors are used [21] with a shift of $0.5e$ from each proton onto the central oxygen atom of the water molecule, as was used in a recent joint x-ray and neutron study of ambient water. [15]

	OO	OH	HH
D ₂ O	0.0374	0.1721	0.1977
HDO	0.0374	0.0378	0.0095
H ₂ O	0.0374	-0.0965	0.0622
H ₂ O (X-ray)	0.323	0.162	0.020
H ₂ O (X-ray modified)	0.329	0.073	0.004

D is substantial and currently there is no known way of correcting for this reliably. As a result a variety of empirical schemes are adopted, which normally involve setting up some sort of polynomial or other smooth function to represent the inelasticity correction. At reactor neutron sources the Q variation is achieved by fixing the neutron energy and scanning as a function of scattering angle. This produces a relatively small inelasticity correction at low Q (low angles), but it gets progressively larger as the scattering angle and Q increases. At pulsed neutron sources the Q variation is achieved by fixing the scattering angle and scanning in neutron wavelength. Provided the scattering angle is not too large, this alleviates the problem with the high Q correction, but now the correction tends to diverge at low Q , and is much worse for H compared to D because of the lighter mass and much larger incoherent cross section of the proton.[22]

It is not appropriate here to go into a lengthy discussion of these corrections for either x-rays or neutrons. It will be assumed that for the various types of diffraction experiments appropriate corrections for inelasticity and other systematic effects, such as sample attenuation and multiple scattering, can be performed [23]. Even so different experimentalists often have different methods of correcting their data, so that, due to uncertainties in these corrections, independent experiments on the same material under the same conditions do not necessarily yield identical data.

It is also should be mentioned that a number of other approaches to determining structure can in principle be adopted, such as extended x-ray absorption fine structure (EXAFS) [24], but to date these have not been widely applied to the supercooled and amorphous states of water. Equally electron diffraction was once combined with neutron and x-ray diffraction to attempt to produce three datasets from which to extract the site-site radial distribution functions for water [25]. The technical difficulties of combining these three very different methods are non-trivial. However electron diffraction is crucially important for studying liquid water at ice surfaces [26–28]

and in microscopic water droplets [29], work that seems to often go unnoticed.

III. INTERPRETING THE STRUCTURAL DATA

Having obtained some data the experimentalist is faced with the tricky task of understanding what it means. For many years there really was only one approach to interpreting diffraction data. Based on the available weights outside each of the OO, OH and HH structure factors, such as given in Table I, the differential cross sections from at least three of the experiments were inverted to yield individual partial structure factors. These were then numerically converted via Fourier transform to give the corresponding site-site radial distribution functions. From the resulting curves coordination numbers and possible local molecular geometries could be calculated. This was the approach adopted in the earlier x-ray [16] experiments on water and was followed in the subsequent neutron experiments [30–33]. In the case where only X-ray data was available, it was assumed the main contribution from OH and HH to the diffraction pattern came from the intramolecular terms, which could be estimated and subtracted, leaving only the OO term [16], or else the OH and HH terms were estimated approximately from independent neutron data [34].

There were at least two drawbacks with this approach. Simple inversion of the data using the weights matrix left little indication of how sensitive the final structure factors were to systematic error in the original data [23, 35]. Secondly direct Fourier transform of diffraction data produces uncertainties related to the finite range of Q in the data, the noise in the data, and the possible but unknown systematic effects from the data analysis. Subsequently maximum entropy methods became available, [36, 37] which helped to avoid some of the problems with finite Q range [38], but the questions of noise and systematic error remained.

In late 1980's the Reverse Monte Carlo method was invented and this heralded a change in the way the inversion was achieved.[39] Now the approach was to perform a computer simulation of the system under investigation, using sensible constraints on atomic overlap. Like conventional Monte Carlo simulation of fluids, atoms are moved in random steps and directions. Unlike conventional Monte Carlo however, the acceptance or rejection of each move is not based on the change of energy of the system, but on the basis of the change in χ^2 , where

$$\chi^2 = \sum_i \sum_Q (D_i(Q) - F_i(Q))^2 \quad (11)$$

and $D_i(Q)$ is the diffraction data for the i 'th dataset as a function of Q and $F_i(Q)$ is the simulated fit to those data. Thus a move is accepted with probability, p , where

$$p = 1 \text{ if } \Delta\chi^2 \leq 0 \\ = \exp(-k\Delta\chi^2) \text{ if } \Delta\chi^2 > 0 \quad (12)$$

and where k is a number which determines how well the simulation fits the data: the larger the value of k , the closer the simulation should fit the data. Hence k plays a similar role to temperature in a classical MC simulation.

RMC played a major role in revising the way diffraction data were analysed, [40], but its application to water [41–43] raises several concerns about whether reliable structures can be extracted for molecular materials in this way. A principle concern is that within the RMC framework, molecules are defined via ‘‘coordination’’ constraints: these are essentially hard-wall constraints that allow an atom to move uniformly within a specified distance range, but it cannot explore the region either side of the walls at all. Yet we know from elementary quantum mechanics that the atoms of a molecule are never constrained in this way, particularly the proton of water molecule, which is subject to significant zero-point uncertainty. Assuming the potential well is harmonic or nearly harmonic, then the distribution of distances is given by the square of the appropriate wavefunction, which will be closely Gaussian in this instance. It is not in any sense a hard wall function. Thus within RMC reliance is placed on the diffraction data to correct for the inadequacies of the starting assumptions. In particular if the wall criteria are too narrow then the proton can never explore the full range of distances compatible with its quantum nature. On the other hand if they are too wide, then the proton may appear too diffuse, which could have the knock-on effect that some other aspect of the structure is modified to accommodate the misfit of the intramolecular scattering.

There is an even more fundamental issue with RMC that rarely seems to be discussed in detail. This is the fact that the structural phase space explored by χ^2 may have nothing to do with the phase space explored by the real material. Within the framework of information theory, RMC is perfectly valid: it is a very natural way to explore distributions of atoms which are consistent with the chosen criterion, in this case χ^2 . Yet there is simply no way of knowing whether, by constraining allowed distributions to this particular criterion, the simulated system explores even remotely the same phase space as the real system, which explores phase space by means of the system energy. To understand what is meant here in more detail it is possible to show [35] that

$$\Delta\chi^2 = -4\pi\rho \int_0^\infty r^2 \sum_i \left[\sum_j w_j^{(i)} \Delta h_j(r) \right] c_i(r) dr \\ + \sum_i \sum_Q (\Delta F_i(Q))^2 \quad (13)$$

where

$$c_i(r) = 2 \sum_Q (D_i(Q) - F_i(Q)) \frac{\sin Qr}{Qr} \quad (14)$$

Here $\Delta h_j(r)$ is the change in the j 'th site-site radial distribution function caused by the atom move and $\Delta F_i(Q)$ is the corresponding change in fit to the i 'th dataset, with

$$\Delta F_i(Q) = 4\pi\rho \sum_j w_j^{(i)} \int_0^\infty r^2 \Delta h_j(r) \frac{\sin Qr}{Qr} dr \quad (15)$$

The sum over j goes over the $\frac{N_T(N_T+1)}{2}$ pairs of atom types, with N_T the number of atom types. In the case of water $N_T = 2$ and the number of pairs is 3, namely OO, OH and HH. (Note that $c_i(r)$ in (13) here should not be confused with the direct correlation function $c(r)$ which appears in the theory of liquids. Note also that a minus sign is missing in equations (17) and (18) of [35].)

The second term of equation (13) is always positive, but the first will fluctuate positive and negative depending on the values of $\Delta h_j(r)$. In order to minimise χ^2 we therefore require $\sum_j w_j^{(i)} \Delta h_j(r)$ in (13) to at least be the same *sign* as $c_i(r)$, otherwise $\Delta\chi^2$ will certainly be positive. Unfortunately, the data, as represented by $c_i(r)$ in (14), will contain artifacts from the finite range of Q over which they are measured, the measuring noise, the fact that the data are discrete and not continuous, and there may be systematic effects from the data corrections as already referred to. Hence there is a very real possibility that $\Delta h_j(r)$ will be biased by these artifacts, which have nothing to do with the true structure of the material. In the worst case these artifacts can prevent the simulation box from proceeding along a true Markov chain in phase space. Instead it can become localised near a particular minimum and never escape from it.

To prevent this happening, a different approach has been adopted, called Empirical Potential Structure Refinement (EPSR) [35, 44, 45]. In this approach a standard Monte Carlo simulation of the system is performed using an assumed 'reference' or 'seed' potential. The difference function $c_i(r)$ or its equivalent is then used to generate an empirical correction to the seed potential and the simulation run again with this perturbation in the potential. This process is repeated a large number of times until the fit approaches the data as close as can be achieved.

The key to the EPSR process is how the perturbation is generated. If a direct transform were performed as in (14) then EPSR would suffer from the same deficiencies as RMC. In practice however a series of Poisson or Gaussian functions are fit to the difference $(D_i(Q) - F_i(Q))$ with aim of capturing the true misfit between simulation and data, but not the noise and other systematic artifacts. The fit is done in Q space, and since these functions have analytic Fourier transforms, the corresponding real space perturbation can be generated directly without a

numerical transform. Of course even this method still has the *potential* to capture some artifacts of the data corrections and noise, but experience to date has found very few cases where the simulation actually sticks at a local minimum, even when simulating stationary materials such as glasses [46]. In addition bonded atom pairs within molecules are given a harmonic force constant, so that the molecules adopt structures consistent with their measurable or known zero-point amplitudes.

Of course none of these methods is perfect - there is no guarantee for example that EPSR samples the correct phase space any more than there is for RMC - and one has to always bear in mind that the information coming from the diffraction experiment is purely pairwise additive, so these methods may not capture all subtleties of the structure correctly. But now at least there are methods in place to identify the degree of uncertainty in extracting structural information, such as radial distribution functions, from diffraction data and examining what effect different starting assumptions have on the outcome.

Having obtained a configuration of molecules which is consistent with a given set of diffraction data, it is possible to interrogate it for structural trends. One such quantity is the spatial density function, [47, 48], $g(r, \theta, \phi)$ which maps out the density distribution of molecules around a central molecule, after averaging over the orientations of those molecules, as a function of distance, r , and spherical polar coordinates, (θ, ϕ) . Since this is a three-dimensional quantity it is usually plotted as a surface contour, with the contour level set by some criterion, such as the percentage of molecules that are included inside the contour.

Another common quantity to display is the so-called bond angle distribution function, which is actually a representation of the three-body correlation function. In this case three atoms, A, B and C say, are said to form a triplet if atom A is within a specified distance range of atom B, and atom C is within another specified distance range of atom B. The included angle $\angle ABC$ is then calculated, and the distribution of these angles, calculated for all of such triplets found in the simulation box, accumulated.

IV. STRUCTURE OF AMBIENT WATER

Before proceeding to discuss the supercooled and amorphous states of water, it is appropriate to consider briefly the current situation as regards the structure of ambient water. Most of the principle references to ambient water structure studies have already been made here. However it is salient that an x-ray study of water by W. Bol in 1968 [49] has been referenced only 20 times in the past 40 years. This paper was written to clarify the situation as regards the different x-ray studies of water that existed at that time. Using a simple but rigorous analysis technique which *does* take account of the effects of truncation in his calculated distribution function, and

1 using models based on known ice structures to analyse
2 the local order, Bol concludes:-
3

4 “In this paper we have come to the conclusion that water
5 at 25 C can be described as a network of molecules linked
6 to each other by hydrogen bonds of length 2.85Å. A frac-
7 tion of 20% of the bonds have been broken, thus leaving a
8 mean number of 3.2 nearest neighbours for each molecule.
9 In addition, each molecule has a mean number of 4.6 van
10 der Waals neighbours. The local situation in water is in-
11 termediate between the situation in low pressure ice and
12 in its high pressure modifications.”

13 With a statement like that, it is tempting to wonder
14 what exactly has been achieved in the intervening 40
15 years! The devil is the detail of course, and whereas Bol
16 refers to “van der Waals molecules”, Narten and Levy
17 [50] refer to “interstitial” molecules. Given that Bol’s
18 analysis is based on comparison with known ice struc-
19 tures, whereas Narten and Levy invoke a structure which
20 is apparently not found in the ices [51], one is tempted
21 to accept the former interpretation more readily.

22 Qualitatively therefore our notion of the local order
23 in water has not changed appreciably in recent times,
24 with the possible exception of the data coming from the
25 x-ray absorption spectroscopy, discussed further below.
26 Instead there seems to have been a relatively intensive
27 search for the three site-site radial distribution functions
28 for water, driven to some extent by the need to have reli-
29 able functions for testing computer simulations of water
30 against. There have been several attempts by this au-
31 thor to measure these functions using the technique of
32 neutron diffraction with (hydrogen) isotope substitution,
33 [32, 38, 52, 53], with the conclusion that while there is
34 broad agreement between the different determinations, it
35 is clear that there remain quantitative uncertainties on
36 both peak heights and positions. The most recent deter-
37 mination [15] used a combination of neutron and x-ray
38 diffraction data, which seems to give the most definitive
39 results so far, but it is now clear that the accuracy of
40 the current distribution functions is limited by the Q
41 range and quality of the available diffraction data. In
42 addition it is conventional, in order to solve the struc-
43 ture, to assume that heavy and light water have identical
44 structures, whereas in fact they almost certainly do not
45 [54–56]. The most recent analyses have at least brought
46 together rather different x-ray [16, 55, 57] and neutron
47 datasets and shown them all to be reasonably consistent
48 with each other.

49 However not all authorities agree that water structure
50 is known even as well as this. The RMC analyses of Pusztai
51 [41, 42, 58] do not seem to yield a consistent set of ra-
52 dial distribution functions for water and it is claimed the
53 existing data are not adequate to do this reliably. On the
54 other hand, as discussed previously, RMC and EPSR are
55 powerful tools for generating structures consistent with a
56 set of diffraction data, and will make structures that fit
57 the data even when the starting assumptions, such as the
58 structure of the molecule and the likely interaction po-
59 tential are inadequate. Another recent review [59], based

on much earlier data, shows general agreement with other
studies, but once again suffers the defect that different
authors use different approaches for analysing their data
and so not surprisingly arrive at somewhat different con-
clusions.

There have of course been a number of other, non-
diffraction, studies of water structure and it is impos-
sible to give these adequate coverage here. For exam-
ple Walrafen studied the near-infrared Raman scattering
as a function of temperature [60] extensively and came
up with the notion that water consisted of two species,
“hydrogen -bonded” and “non-hydrogen-bonded” water.
This matter will be discussed later in terms of the pro-
posed phase transition between low density and high den-
sity amorphous ice.

More recently, Nilsson and coworkers [14] have stud-
ied the x-ray absorption spectrum (XAS) of water and,
by a lengthy analysis involving density functional theory,
controversially concluded that water may not have 3 - 4
hydrogen bonds as had been generally accepted since the
1960’s, but instead consisted primarily of just 2 strong
hydrogen bonds, and 2 much weaker or non-existent hy-
drogen bonds, which would give a more chain-like struc-
ture than the network structure that had traditionally
been implied. Moreover it was subsequently shown that
such a structural model could not be unequivocally ruled
out by the diffraction data [61], although other authori-
ties did not agree [62, 63]. Following the publication of
the *Science* article there were some attempts to calculate
the XAS spectrum of water [64, 65] with the aim of dis-
counting the 2 hydrogen bond scenario, although these
efforts seemed primarily to highlight the difficulty of cal-
culating of the XAS spectrum for water, rather than to
resolve the controversy. More recently [66] Leetma *et al.*
showed that the symmetric and asymmetric models
of Soper [61] gave very similar XAS spectra when calcu-
lated according to their methods and claimed this was
due to “unphysical” features of both models.

The present author however takes a much different
stance concerning this analysis of Leetma *et al.* Given
that the original claim that water had only 2 strong hy-
drogen bonds was based solely on the XAS data, it seems
very strange that the calculated XAS for the symmetric
and asymmetric models of [61], which represent radically
different local water structures, should look so similar,
irrespective of whether either model is “physical” or not.
Surely a more rational explanation would be either a) we
do not yet know what the XAS spectrum for water is
telling us about the local order in water, or b) we do not
yet know how to accurately calculate the XAS spectrum
of water from a given set of water coordinates? Either
way the conclusions from [14] seem premature at this
time, and for the purposes of the rest of this article, it
will be assumed the conclusions of W. Pol in 1968 quoted
above still apply. Whilst it may be true that diffrac-
tion studies do not formally prove that water is locally
tetrahedral, equally they do not prove it is *not* tetrahe-
dral, and the tetrahedral model fits well with the various

structures of ice, where tetrahedrality is proven beyond all reasonable doubt. Indeed it is difficult to see how any potential model for water which treats the two protons identically and which reproduces the experimental site-site radial distribution functions for water can ever give a structure which is not tetrahedral in its local environment. No doubt this debate will run for some time yet but it is to be hoped that in the near future sufficiently definitive experimental and theoretical evidence will become available to resolve the matter once and for all.

V. SUPERCOOLED AND CONFINED WATER

Study of water below its normal freezing point is intrinsically much more difficult than above in the stable liquid phase, since the water must be extremely pure and contained in such a way that there are no inhomogeneities to trigger ice nucleation. As a result the number of detailed structural studies of supercooled water is far smaller than of the ambient liquid. To prevent freezing samples are typically contained in thin, smooth walled silica capillaries, various porous materials such as vycor glass [67], MCM-41 silica [68, 69], carbon nanotubes [70], activated carbon pores [71, 72] or held in an emulsion [73]. This has so far prevented detailed structural analysis of the neutron diffraction experiments using isotope substitution, except for one case where the [74] site-site radial distribution functions were measured for slightly supercooled water (-5°C), and shown to be consistent with previous measurements at the same temperature but at higher pressure in the stable liquid phase [3]. A significant concern with these measurements is that as the degree of confinement is increased to prevent freezing, the water becomes progressively less bulk-like, and water-substrate interactions start to influence both the structure, dynamics and thermodynamic functions.

The structure of highly confined water has been studied by both x-rays, [71, 72], and neutrons [71, 73, 75]. In these studies except [75] it is assumed the substrate-water correlations can be ignored, which, given the substantial degree of confinement involved, is a questionable assumption. A general pattern to emerge from the x-ray studies is that the diffraction pattern from water in confinement changes in a manner which closely resembles what happens to pure water under pressure, [76], namely the second peak in the x-ray radial distribution function moves inwards, signalling a marked degree of hydrogen bond bending in confinement. The neutron patterns are less clear, primarily because of the different correlations that contribute to this pattern and due to the significant truncation oscillations that occur in the Fourier transformed diffraction patterns, but at high pressure and low temperature the neutron diffraction pattern from heavy water appears closer in shape to that of high density amorphous ice (HDA) than to low density amorphous ice (LDA) [73]. Even at ambient pressure and 77K the neutron diffraction pattern in confinement resembles that

of HDA [71], but with the main peak shifted to lower Q values. The X-ray diffraction patterns under the same conditions are not shown, but the x-ray radial distribution function under the same conditions appears closer in form to LDA than HDA (Figure 10 of [71]). Once again, however, given the high degree of confinement involved in these studies and the fact that surface-water interactions are ignored, there has to be some concern about whether the observed trends have anything to do with bulk water.

A later study goes further than these, by exploring the dynamics as well as the structure, [67]. In this case the neutron diffraction pattern is observed in 25% hydrated vycor glass as a function of temperature. Under these conditions water apparently does not freeze all the way down to 77K. Between 238K and 258K the main peak in the neutron diffraction structure factor shifts rather abruptly from 1.86\AA^{-1} to 1.71\AA^{-1} , accompanied by signals in the DSC traces, but the rest of the diffraction pattern still looks similar to bulk supercooled water at 260K. The peak does not move again all the way down to 77K. There are no x-ray data shown to accompany this apparent transition, and it is stated:

“In hydrogen-bonded liquids, the FSDP position can be related to the density of the system and may be considered as an index of the structure.”

Indeed it is claimed that the peak shift corresponds to a change in structure from a low density form to a high density form.

What is strange here is that the first peak in HDA occurs at 2.08\AA^{-1} , not at 1.86\AA^{-1} as in confined water. Hence if we are to believe the first peak position is a measure of density, this is still a long way from being the density of HDA. Moreover even at 77K with the main peak at 1.71\AA^{-1} , the neutron diffraction pattern still does not look like LDA, 2, but rather more like HDA. See Figure 2.

In general it is not possible to relate the position of a single peak in a disordered material's diffraction pattern to either density or structure. This is true even in a crystalline sample. Consider the simple example of hexagonal close packing compared to cubic close packing. For a given interatomic spacing they will have identical number densities. Even the first diffraction peak is at the same Q value. But the height of that peak will be different between the two structures, and the heights and positions of all the subsequent diffraction peaks will also be different. So it would be very unsafe to infer the structure from one peak alone. In addition density is not well recorded in the diffraction pattern, since there is always the possibility of lattice site vacancies, which will not be obvious without careful analysis of all the peaks.

One particular concern about the peak shift reported in [67] is the question of whether the sample has crystallised or not. Given that the sample consists of a monolayer of water on a very non-uniform substrate, there would be substantial particle size broadening of any crystalline peaks that might occur in the diffraction pattern. Hence a crystallisation transition might not yield sharp

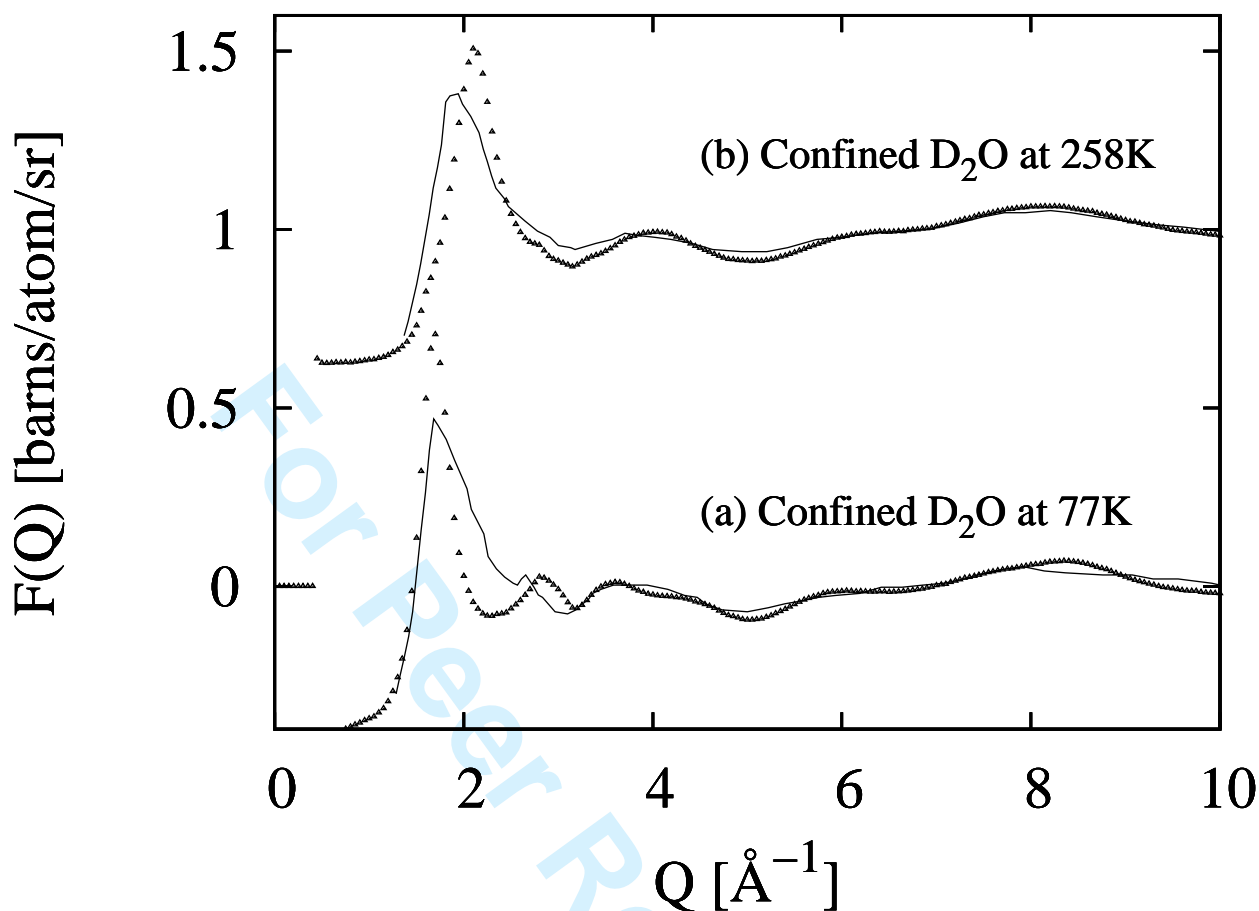


FIG. 2: The differential cross section of highly confined heavy water obtained by Zanotti *et. al.* at (a) 77K and (b) 258K, (lines, [67]). Also shown are the diffraction data for (a) LDA and (b) HDA (triangles, [77]). It is apparent that at 258K the first peak of the confined water does not coincide with that of HDA, and that at 77K the structure beyond the first peak in confined water does not match that seen in LDA.

Bragg peaks, but it might yield the sudden shift in peak position that is observed in these data. Without more information, the verdict has to remain open on this issue.

Yamaguchi *et. al.* [72] do see clear Bragg peaks on cooling below 258K, with corresponding features in the DSC trace. However this latter case is almost certainly at a higher water coverage than the water in vycor data. In another example of water in MCM-41, a sharp freezing transition is observed by x-ray diffraction in highly confined water at about 235K [78] in two out of three samples that were tested. For the third, narrower pore sample (sample 2) the crystallisation appeared to occur over a much broader temperature range, suggesting the observed narrowing of the main diffraction peak was highly dependent on the particular sample concerned.

For these reasons therefore there have to be serious question marks around the issue of what exactly is the nature of the water in these highly confined environments and whether it has anything to do with the bulk liquid

that would exist if it could under these conditions.

An even more contentious debate has arisen over the dynamics of confined water. By means of a series of small angle neutron scattering (SANS), quasi-elastic neutron scattering (QENS) and NMR experiments, Chen and coworkers have studied confined water in a number of different environments, [8, 67, 68, 70, 79–91]. By analysing the QENS line width [8] and NMR relaxation times [83] of water in MCM-41, it is concluded that confined water undergoes some form of fragile to strong (FS) transition at 225K. This transition is plotted as a function of pressure, [8] and shown to move towards the purported second critical point of water, at about 0.16GPa and 200K. Apparently there are no observable transitions at higher pressures. It is speculated that the line of FS transitions corresponds to the so-called Widom line, which is the extension of the HDL/LDL coexistence line into the single phase region above the critical point.

There are however a number of questions about this work that need to be elaborated. Firstly Mallamace *et.*

1 *al.*, as part of their justification for using MCM-41 for
 2 this study state [83]:

3 “In particular, the XRD data [78] give, for the first
 4 sharp diffraction peak of water, the following results: wa-
 5 ter in MCM-41 with a pore diameter $d = 42\text{\AA}$ shows a
 6 sudden freezing at 232K, whereas for $d = 24\text{\AA}$ it remains
 7 in a liquid state down to 160 K.”

8 Yet in reference [78] Morishige and Nobuoka go to some
 9 lengths to demonstrate that they believe the slow tran-
 10 sition they see at $\sim 230\text{K}$ for the confined water in the
 11 24\AA diameter pore is in fact a slow freezing transition,
 12 the slowness being induced by the high degree of confine-
 13 ment. Quoting some previous NMR studies they state:

14 “Recent NMR studies ... of the pore water confined
 15 in purely siliceous MCM-41 have revealed that on cooling
 16 the mesoporous materials with pore diameter larger than
 17 $\sim 3\text{nm}$ below the bulk freezing temperature the free water
 18 first freezes abruptly and then the bound water freezes
 19 very gradually at lower temperatures $\sim 220\text{--}180\text{ K}$.”

20 The evidence presented in that paper can hardly be
 21 regarded, therefore, as conclusive proof that the water in
 22 these narrow pores is still liquid down to 160K. Hence
 23 there seems to be a discrepancy between the claims of
 24 Mallamace *et. al.* on the one hand, and of Morishige
 25 and Nobuoka on the other. At best the x-ray data may
 26 indicate there is a monolayer of “unfreezable” water be-
 27 tween the water at the centre of the pore and the silica,
 28 whatever that means. However they assume this water to
 29 be highly disordered and possesses little “short range” or-
 30 der, since it apparently does not contribute to the diffuse
 31 diffraction pattern. The observations from this earlier
 32 x-ray work in fact appear to be closely parallel to those
 33 seen with neutrons [67].

34 In addition both Cervený *et. al.* [92] and Swenson
 35 [93] have issued comments on Liu *et. al.*[8]. Cervený *et.*
 36 *al.* argue that the observed FS cross over is in fact due
 37 to the onset of confinement effects and quote several re-
 38 lated cases of confined water where the same behaviour
 39 in the QENS data has been seen, and also quote the case
 40 of polymer blends where the same trend is seen. Swen-
 41 son argues that if the QENS data are taken literally they
 42 would extrapolate to a glass transition temperature of
 43 50K, which would be unacceptably low. Like Cervený *et.*
 44 *al.* he also argues that what the QENS data are seeing is
 45 the effect of confinement killing the α relaxation process
 46 in water, rather than any FS transition. Subsequently
 47 Swenson and coworkers have published a dielectric re-
 48 laxation of study of water highly confined in MCM-41
 49 [94]. They observe no obvious transition from Arrhen-
 50 ius to Vogel-Fulcher-Tammann (VFT) behaviour in the
 51 dielectric relaxation time of the water as a function of
 52 temperature, particularly at the temperature where this
 53 transition occurs in the QENS and NMR data.

54 In response to these comments, Chen *et. al.*, [95], cite
 55 neutron spin echo measurements which measure the col-
 56 lective dynamics of the protons as showing similar ef-
 57 fects to the QENS data, and also cite additional ambient
 58 pressure QENS data at even smaller pore sizes where

the transition is seen at the same temperature. They
 also draw on computer simulation evidence, and disagree
 that the effect is due to the α relaxation becoming non-
 observable.

There currently appears to be no satisfactory resolu-
 tion to the discrepancies in the interpretations of the
 different experimental results. What is almost certainly
 true at the current time is that we do not yet have a
 coherent picture of what is actually going on in confined
 water at low temperatures, so that statements about ob-
 servation of a fragile to strong transition are probably
 premature at this stage. It is also not obvious whether,
 given the highly confined nature of the water required to
 observe these effects, the existing results have anything
 to do with bulk water as it would be if it did not crys-
 tallise under these conditions. In order for the water to
 go into the pores in the first place there must be reason-
 ably marked interactions with the wall atoms, and all the
 evidence points to water being strongly modified in struc-
 ture inside a pore, [71, 72, 75]. Such interactions were
 also clearly visible in an independent study of methanol
 in MCM-41 [96]. Current interpretations of the dynamics
 data seem to ignore this fact.

The above survey may not cover all aspects of this
 problem, but it certainly gives a flavour of the disparate
 accounts that are currently in the literature.

VI. AMORPHOUS SOLID WATER AND AMORPHOUS ICE

At even lower temperatures than the case of super-
 cooled and confined water, that is around 150K or below
 it is possible to study water only in the glassy or amor-
 phous states. Initially amorphous water was produced in
 its low density form either by vapour deposition onto a
 cold substrate [97], or by hyperquenching small droplets
 of the liquid [98, 99]. Subsequently Mishima *et. al.*
 [100, 101] showed that high density amorphous ice (HDA)
 could be obtained by compressing ice Ih smoothly at 77K
 to above 1GPa. This solid was then shown to be formed
 by pressurising low density amorphous ice (LDA) to \sim
 0.6GPa in what appeared to be a first order phase tran-
 sition [102]. At that time the idea of a reversible first-order
 phase transition between two amorphous states was rela-
 tively new, and, not surprisingly given the importance of
 water in many different fields of science, it sparked a huge
 effort to try to understand its properties, and to identify
 the underlying causes of this rather sudden transition.

Much later it was shown that by annealing at 1.1GPa
 up to 165K HDA could be reversibly converted to a more
 dense form of HDA, called VHDA [103], although there
 was no indication that the transition was sudden as in
 the case of LDA to HDA. Indeed it was surmised there
 might be a continuity of states between HDA and VHDA.

The earliest reported structure determination of amor-
 phous ice was by Narten *et.al.* using x-rays on the vapour
 deposited form [104, 105]. In the second study they ac-

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tually studied 3 samples, one deposited at 10K and measured at 10K, the second deposited at 10K and measured at 77K, and the third deposited and measured at 77K. The structures obtained were rather different between the three samples, with a pronounced second peak in the radial distribution function at $\sim 3.3\text{\AA}$ in the samples deposited at 10K not present in the sample deposited at 77K. This already suggested that depositing at 10K gives rise to a distorted structure which needs to be annealed to obtain the equilibrium structure. In fact Jeniskens [26] later identified by electron diffraction this low temperature structure as a form of (probably highly non-annealed) HDA.

Subsequently Bosio *et al.* measured the x-ray diffraction pattern of HDA obtained by compressing ice Ih, and LDA obtained from HDA by heating [106, 107]. For LDA the diffraction pattern was closely similar to that of Narten for the sample deposited at 77K, and there was a clear distinction in structure between HDA and LDA. The main effect is that the second peak in the x-ray radial distribution function (which is dominated by the OO correlation in this case - see Table I) at $r \approx 4.5\text{\AA}$ splits into two peaks, the first at $\sim 3.5\text{\AA}$ and the second at $\sim 4.5\text{\AA}$, while the first peak in the same radial distribution function barely moves. Together with this came neutron diffraction data on the same materials [108], which highlighted the changes in the hydrogen bond network in going from LDA to HDA. Subsequently the structure of hyperquenched glassy water (HGW) was studied by both x-ray and neutron diffraction [109], where it was shown to be closely similar in form to LDA.

Later still Finney *et al.* measured the structure of LDA and HDA [110] and VHDA [111] using the technique of hydrogen isotope substitution, as described in section II of this review. In this case and probably for the first time the data analysis was supplemented with a computer simulation technique called EPSR as described earlier, allowing a more detailed interrogation of structural models which were consistent with the data. It was proposed that the primary structural change between LDA, HDA and VHDA was the collapse of the second coordination shell inwards and towards the first, in a manner which was closely analogous to what had been seen in the stable liquid phase, [3] as a function of pressure, see section VII. Subsequently Klotz *et al.* measured the structure of amorphous D_2O ice *in situ* under pressure [112], and although isotope substitution was not available in this case and the data were available over a much narrower Q range, computer modelling of the data seemed to give a similar picture of the structure as amorphous ice was compressed. Most recently the same analysis procedures have been extended to amorphous solid water (ASW) (produced by vapour deposition) and HGW, [77]. Here it was shown that ASW, HGW and LDA are very similar in structure, while HDA and VHDA are quite distinct.

There has been a significant debate about the true nature of amorphous ice. Is it amorphous or is it really a highly disordered crystal? Are the different forms of

amorphous water, e.g. ASW, HGW, LDA truly equivalent? Do HDA and LDA connect continuously with their high and low density liquid analogues near to ambient temperatures? Arguing on the basis of thermodynamic and dynamics evidence, Johari presents a comprehensive series of studies of the transformations between different amorphous ices, [113–120]. In particular it is believed that at 140K amorphous ice behaves as a very viscous liquid, rather than a true glass, [114, 118]. Moreover there are questions about whether HGW and ASW and LDA are equivalent in the thermodynamic sense, even though they appear structurally equivalent [115], which raises issues about how these states relate to the phase diagram of water in the stable liquid and supercooled regime. The same theme is taken up independently by Tse *et al.* [121] and Shpakov *et al.* [122] where a combination of inelastic neutron scattering, RMC, molecular dynamics and lattice dynamic calculations are used to show that there may be a discontinuity between LDA and supercooled water, both energetically and structurally. In particular it was shown that the transformation of ice Ih to HDA is a form of mechanical melting rather than true thermodynamic melting, [121], questioning therefore whether LDA and HDA should correctly be regarded as low temperature counterparts of the higher temperature low density (LDL) and high density (HDL) liquids.

Another significant question concerns whether the transition LDA to HDA can be regarded as a discontinuous phase transition, or is it in fact continuous? In his original paper, Mishima is clearly of the view that the transition is discontinuous, and more recently he has followed this up with a Raman and visual study of the transformation, [123] which also strongly hints that the transition is rather sharp. However in a paper in Science in 2002 [124] Tulk *et al.* come to a different conclusion. They follow the transition of recovered HDA to LDA by heating the sample in steps through 110K. Following each annealing, the sample temperature is lowered to 40K and a diffraction scan performed. It is noteworthy that the time taken for the full anneal is significantly longer for the x-ray scans (~ 4000 mins) compared to that for the neutron scans (~ 1200 mins), and the first peak moves further for each anneal in the neutron scans compared to the x-ray scans. Whilst the first peak in the neutron and x-ray patterns corresponds to different correlations, the difference in timing of these anneals seems to suggest the neutron and x-ray samples are not identical. At each anneal they capture the structure in a series of intermediate stages and show that, particularly at 105K, it cannot be reproduced by a simple arithmetic combination of the end point structures. This would appear to rule out the possibility of a truly first-order transition from HDA to LDA, although given Narten's earlier experience with different amorphous ice structures being produced by different deposition temperatures [105], there has to be some question about the effect of cooling the sample to 40K in order to perform the diffraction scans, since as we saw with the Narten work doing so might induce

1 structural anomalies.

2
3 New versions of this work appeared subsequently [125–
4 127] which amplified on the earlier *Science* conclusions
5 with more diffraction scans, using just x-ray diffraction
6 in this case, and accompanied by MD simulation, which
7 seemed to show the same trends. They also showed a
8 graph of the splitting of the main peak in the x-ray radial
9 distribution function, and how it merges to form a single
10 peak in the LDA phase [127]. The temperature range
11 for the transition was in fact quite narrow, somewhere
12 between 110K and 115K.

13 Independently, Nelmes and coworkers [128] undertook
14 detailed, in situ studies of amorphous ice under pressure,
15 using both neutron diffraction and Raman scattering.
16 Here they showed clearly that as one went through the
17 transformation HDA to LDA *under pressure*, the diffraction
18 patterns appeared to be exactly reproducible as the
19 linear combination of those of the end point structures.
20 Raman scans at different points in the sample during the
21 transformation appeared to show distinct patches of LDA
22 and HDA, in support of the diffraction scans. Their con-
23 clusions were therefore different from Tulk *et. al.*, namely
24 that the transition HDA to LDA was indeed first order.

25 Commenting on the Klotz *et. al.* work [128], Tulk
26 *et. al.* [129] show that the neutron diffraction experi-
27 ment may be rather insensitive to the underlying network
28 structure of the ices due to the strong component of OH
29 and HH correlations in the neutron data: if x-rays had
30 been used there might have been a different conclusion.
31 In reply Klotz *et. al.* [130] state that

32 “An interpretation in terms of a continuum of interme-
33 diate states would require a sequence of such states (i)
34 that were amorphous ices somehow intermediate between
35 LDA and HDA and yet gave such strangely different pro-
36 files from the end members; (ii) that nevertheless just
37 happened to mimic a resolvable two-state behavior, this
38 closely, through the whole sequence; and (iii) that also
39 managed to mimic the expected pressure behavior of a
40 two-state system so exactly through the whole sequence.
41 This is extraordinarily improbable.”

42 The wording of this last sentence is questionable. If the
43 materials had been a mixture of two crystalline phases,
44 e.g. ice VI and ice Ih, then there would be two dis-
45 tinct sets of Bragg peaks superimposed, corresponding to
46 the distinctly different long range orders for each mate-
47 rial. Hence one could unambiguously say there were two
48 phases present and they were transforming discontinu-
49 ously from one to the other as the peak intensities from
50 one structure grew at the expense of the peak intensi-
51 ties from the other. For a glass or liquid, especially in
52 this case looking at a single, diffuse diffraction peak, the
53 story is quite different, and rather than being “extraordi-
54 narily improbable”, an intermediate state can quite eas-
55 ily appear to be a linear combination of its end points
56 in a disordered material and still be monophasic. The
57 condition that the diffraction pattern be the mean of its
58 end structures is a necessary requirement for two dis-
59 tinct structures to exist through the transition, but it

60 does not constitute proof that distinct structures actu-
ally exist [131]. In the next section it will be shown that
the case of the transformation of high density to low den-
sity water in the stable liquid region is a situation where
exactly this appears to happen. This of course is not to
say that the transformation HDA to LDA is not discontin-
uous, simply that in a formal sense the behaviour of
the main diffraction peak with density cannot be used to
conclude this.

So how can we distinguish between these two views,
namely is the transformation HDA to LDA discontinu-
ous or continuous? Probably, given the metastable na-
ture of both materials we will never have a totally clear
cut answer. However in subsequent work Nelmes *et. al.*
explore the amorphous phase diagram in more detail
[132], possibly more so than has been achieved by
other workers. Here they identify an annealed form of
HDA, called e-HDA, which appears to transform discontin-
uously to LDA. In particular the recovered form of
e-HDA transforms to LDA at a much higher tempera-
ture >120K, which also implies it is a more stable form
of HDA. In this case on heating recovered e-HDA after
annealing at 0.18GPa (a) and at 0.30GPa (b), the main
diffraction peak stays almost constant up to 128K (a)
and 122K (b), but at 130K and 125K respectively, i.e.
with a temperature increase of just 2-3K, both samples
transform to LDA. Moreover they show that e-HDA can
be reversibly transformed into VHDA, suggesting that
e-HDA is in fact the stable high density form of amor-
phous ice, and that other forms of HDA are linked to it
reversibly and continuously. There was very little hint in
this second study of intermediate states as in the previous
study [128]. This second set of findings seem to fit in with
those of Koza *et. al.* previously [131], where, although
the transition occurred at lower temperatures near 100K,
they observed a gradual evolution of the diffraction pat-
tern until at some point it transformed discontinuously
to LDA. Thus it seems that correctly annealing the sam-
ple is a crucial step in trying to produce the most stable
form of HDA.

What does seem clear from all these accounts, aside
from the question of whether the transition is truly dis-
continuous or not, is that the transition certainly occurs
over a very narrow temperature range. At the very least
one should say it is “first-order-like” even if it is not ac-
tually first order. No doubt, however, precise views on
this will differ from researcher to researcher.

All the work referred to above concentrates on the
main peaks in the diffraction pattern, corresponding
primarily to the local order around individual water
molecules in the glasses. So far there has been no refer-
ence to what might happen at longer distance ranges,
as manifest in the small Q scattering. Clearly any trans-
form from one state to another might involve significant
heterogeneities during the transition if it were discontinu-
ous. Here the work of M. Koza and colleagues has yielded
some insight, [133, 134]. Using small and wide angle neu-
tron scattering they watch the in situ transformation of

1 HDA to LDA. In particular it appears that the main
2 diffraction peak evolves continuously through the transi-
3 tion, becoming markedly broader in a state labelled SSH,
4 which corresponds to the “structure of strongest hetero-
5 geneity”. This state is also indicated by the marked in-
6 creas in small angle scattering around $Q = 0.1\text{\AA}^{-1}$. The
7 authors caution against assigning this directly to the ex-
8 istence of a mixed phase system, although they do rule
9 out the possibility of the transformation being homoge-
10 neous. Once again the transformation HDA to LDA they
11 observe occurs over the temperature range 100 - 105K,
12 implying it is fast even if not sudden.

13 One salutary comment about all of this work is that
14 different authors insist on doing their experiments in dif-
15 ferent ways and under different conditions, which means,
16 given the non-equilibrium nature of the structures, it is
17 almost impossible to make direct comparisons between
18 the different results. Fortunately the work of Nelmes
19 and colleagues has recently been revisited by Winkel *et*.
20 *al.* [135], who also conclude that under decompression,
21 VHDA transforms continuously to e-HDA, then there is
22 an abrupt transition to LDA at about 0.06GPa, with
23 no intermediate states. No doubt the phase diagram of
24 amorphous ice will continue to intrigue experimentalists
25 for many years to come!

26 VII. THE NATURE OF THE STRUCTURAL 27 TRANSITION IN WATER

28 Perhaps the most common phase transition of all, the
29 melting of a crystal into a liquid, typically occurs with
30 a pronounced density change and absorption of latent
31 heat, causing a dip in the differential scanning calorime-
32 try (DSC) profile. Structurally, the transition is marked
33 by a rapid disappearance of Bragg peaks, caused by the
34 long range order in the material, from the diffraction
35 profile, to be replaced by a few broad diffuse scattering
36 peaks, arising from the now only local order in the liquid.
37 This latter order normally proceeds only a few molecular
38 diameters into the liquid, then disappears. On the other
39 hand the transition of a liquid to its vapour, whilst being
40 very visible in the form of boiling, actually does not make
41 a radical change in the diffraction profile: such diffrac-
42 tion peaks as can be seen in the gas state are still very
43 diffuse and certainly not sharp in any sense. For the case
44 of liquid water in the dense gas phase see for example
45 the neutron diffraction work [136], where the diffraction
46 pattern does not look qualitatively different to that in
47 the condensed phase [15]. The point is of course that
48 because the liquid-vapour transition line in the pressure-
49 temperature phase diagram ends in a critical point, it
50 is always possible to pass from the dense liquid to the
51 vapour by going around the critical point and so avoid
52 the liquid to vapour phase transition. This is never true
53 of the crystal to liquid transition which is always first
54 order at any pressure as far as we know.

55 A well known example of a liquid transforming rather

56 abruptly to another liquid is the case of liquid sulphur.
57 When sulphur is heated to 383K it melts to form a low
58 viscosity liquid which flows quite easily, but heat it some
59 more, above 431K it suddenly becomes very thick and
60 viscous. This transition is believed to be due to the
formation of long chains of sulphur atoms at the higher
temperature. Yet the density barely changes in the trans-
formation, (0.0335 atoms/ \AA^3 before to 0.0332 atoms/ \AA^3
after) and the diffraction patterns for sulphur in these
two different states are almost identical [137]. Hence
diffraction from a disordered material cannot by itself
necessarily tell us the state of the material, unlike crys-
talline phases, where each phase has a distinct sequence
of Bragg peaks.

The diffraction pattern for heavy water in the ambient
and supercooled phases has been studied extensively by
Bellissent-Funel *et. al.* [73], and used to look for trends
in peak positions with temperature and pressure. Later
Bellissent-Funel analysed these results in terms of a two-
state model, assuming the diffraction pattern at some in-
termediate state could be represented as the linear com-
bination of the diffraction pattern at the two endpoints,
namely high density liquid (HDL) and low density liquid
(LDL), [138]. The same idea was taken up over a much
more limited set of pressures and temperatures in the sta-
ble liquid region at 268K over a pressure range 0 - 0.4GPa
[3]. Figure 3 shows the heavy water diffraction data from
those experiments, measured at densities 0.1016, 0.1087
and 0.1142 atoms/ \AA^3 together with the projected data,
derived by linear extrapolation of the experimental data,
for two fictitious densities, one (assumed to be LDL) well
into the negative pressure region of the phase diagram at
0.0885 atoms/ \AA^3 , and the other (assumed to be HDL)
well into the crystalline region of the stable phase di-
agram at 0.1206 atoms/ \AA^3 . These densities are com-
parable with the densities of LDA and HDA at much
lower temperatures. All five datasets were analysed us-
ing EPSR simulation, with 2000 water molecules in a
cubic box of the appropriate dimension, and all other
simulation conditions exactly as described in [15]. The
simulations shown here are new in that the total neutron
differential cross sections (equation 2) have been anal-
ysed here, instead of the partial structure factors derived
from those data, as in [3].

Figure 4 shows the OO partial structure factors ob-
tained in these EPSR simulations, while figure 5 shows
the respective OO site-site radial distribution functions
from the same simulations. We note from the structure
factors that there is no sign of increased scattering at low
 Q in the “mixture” samples, (b), (c) and (d). Hence, at
least within the limitations and range of the data and
computer simulation there was no sign of the structural
heterogeneity that was seen experimentally for the trans-
formation from HDA to LDA [134]. In r -space the first
peak is seen to be almost stationary with density, while
the second peak, which is at $\sim 4.5\text{\AA}$ in LDL moves to,
or is replaced by a peak at $\sim 3.5\text{\AA}$. For the intermedi-
ate states (c) and (d) we note that this peak appears to

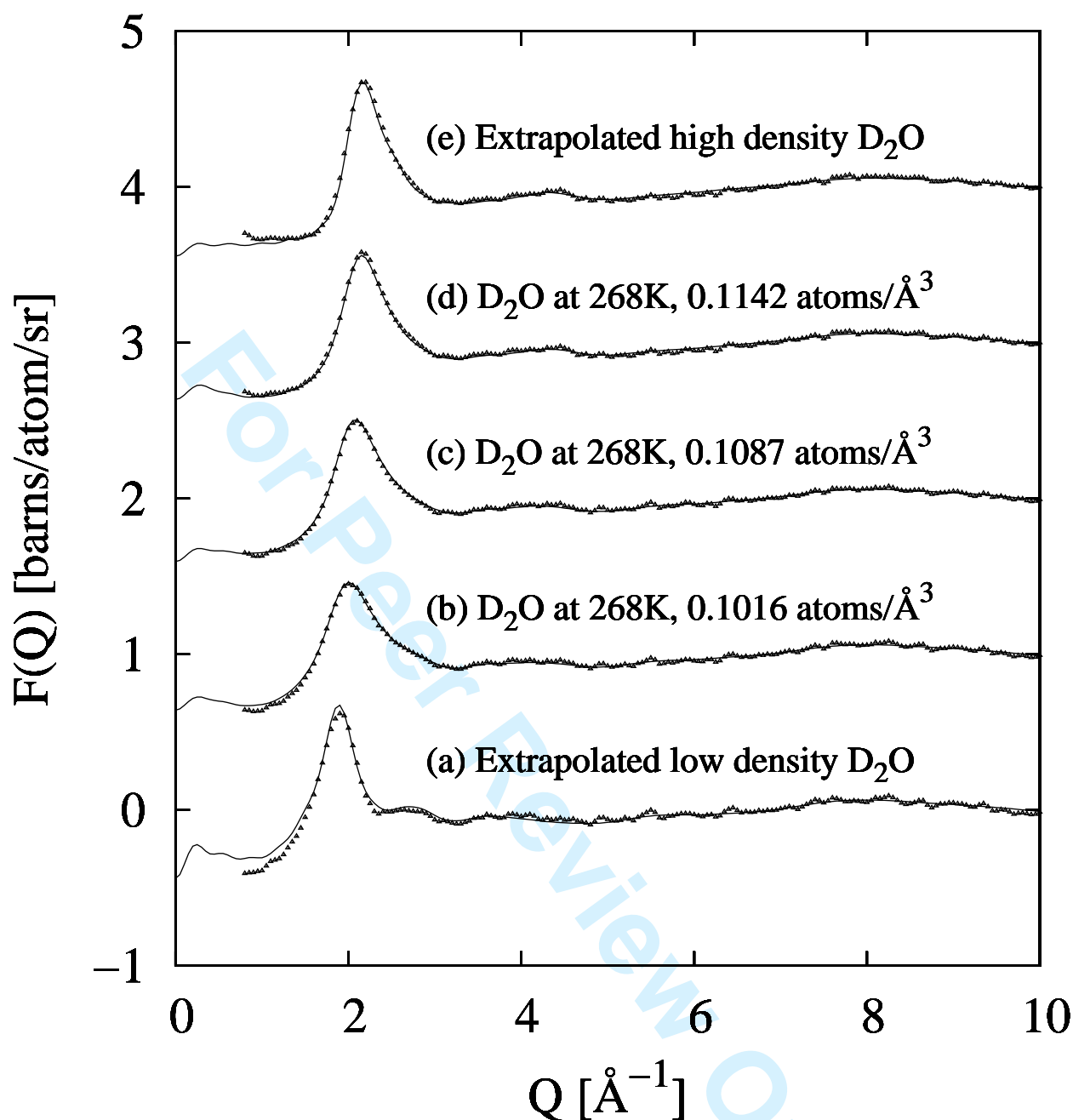


FIG. 3: The differential cross section of heavy water at 268K at three measured densities, as well as extrapolated data to low and high density. (a) is the extrapolated LDL at $0.0885 \text{ atoms}/\text{\AA}^3$, (b) - (d) are the experimental data at densities 0.1016 , 0.1087 and $0.1142 \text{ atoms}/\text{\AA}^3$ respectively, and (e) is the extrapolated data to $0.1206 \text{ atoms}/\text{\AA}^3$. From [3]. The lines show the EPSR fits to these data. Note that the qualitative differences between LDL and HDL as shown in (a) and (e), linearly extrapolated from the measured data at intermediate densities, are mirrored in the data for LDA and HDA, Fig. 2. Note that the statistical quality of these data is much worse than for the amorphous ices because of the large ($\sim 95\%$) contribution to the scattering from the pressure containment cell which has to be subtracted in the data analysis.

split, in a way closely analogous to that observed by Tulk *et. al.* [127]. Indeed figure 6 shows the position of the second peak as a function of density, and it is seen that this peak movement or growth is not uniform with density increase. On the contrary, with increasing density

from 0.0885 to $0.1016 \text{ atoms}/\text{\AA}^3$ the peak barely moves, but becomes markedly broader, while at higher densities it rapidly collapses towards the first peak. Meanwhile the larger r structure also collapses inwards - see Fig. 5. Although the details will be slightly different in individ-

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ual samples, this is exactly the same underlying trend that is seen going from HDA to LDA, [127, 139]. Hence, notwithstanding the observation that LDA is not necessarily contiguous with the supercooled liquid, [115, 121], it is clear that their underlying structures are nonetheless closely related, and this observation applies to the comparison of HDL with HDA as well.

Figure 7 shows the coordination number of the first OO peak out to 3.15\AA - this is the position of the first minimum in HDL - and of the second peak from 3.15\AA to 4.00\AA as mentioned in section IV with reference to the work of Bol [49]. Once again it is seen that while the first peak coordination number increases by about 32% in this density range, the second distance range, which becomes the second peak in HDL, more than doubles its coordination number over the same density increase, which is about 36% greater for HDL compared to LDL. This marked change can only occur if the O-O-O bond angles, which are centred close to the tetrahedral angle in LDL, become much more bent in HDL - see Fig. 8. The transition here is not discontinuous, but it is relatively sharp with increasing density and one could imagine hypothetically if we could go down in temperature, then it might become discontinuous, just as for the supercritical gas the density change with pressure becomes increasingly rapid as the temperature is lowered, becoming discontinuous once the temperature falls below the critical point. In the present case however, the low density liquid lies in the negative pressure part of the phase diagram, which makes the experimental difficulties of performing diffraction experiments seemingly insurmountable!

VIII. RELATIONSHIP TO THE PHASE DIAGRAM OF WATER

The focus in this article so far has been on experimental results on the supercooled and amorphous states of water, with particular emphasis on the structure of these materials. When discussing the phase diagram of water, it is essential to distinguish the hypothetical phase diagram of water derivable from computer simulations and theory of water, from that of the real substance. In fact, due to the fact that it crystallises so readily, very little is actually known about the phase diagram of water below the homogeneous nucleation temperature [2]. Therefore what follows is related more to what is conjectured to be the phase diagram of water if crystallisation could be inhibited, than to the actual phase diagram of water at low temperature. It is tacitly assumed this hypothetical low temperature phase diagram joins continuously with the known phase diagram of water in the supercooled and stable liquid regions.

The idea that water might have a second critical point was first mooted in 1992 when Poole *et. al.* [141] showed that the line of temperatures of maximum density did not intersect the liquid spinodal for the ST2 potential model of water. Instead below this second critical point water

would undergo a phase separation into two forms, the HDL and LDL as already discussed, and it was proposed that HDA and LDA were the low temperature extensions of these liquids, as mentioned in the introduction. Later Mishima and Stanley measured the melting curve of Ice IV and Ice V and this was used as evidence for, but it did not prove, the second critical point hypothesis, [11, 142]. Above the conjectured second critical point in the P-T plane would lie the “Widom” line where thermodynamic response functions such as the isobaric heat capacity would reach a maximum [143], so that even if the second critical point itself was not observable, its influence would be seen in the thermodynamic properties of the stable liquid region.

Alternatively, the “singularity-free” scenario [144] did not propose a second critical point as such, but nonetheless invoked the possibility of a continuous but sharp transition at low temperature between LDA and HDA. Theoretical studies of a “simple” model which showed both types of behaviour suggest that the change in bonding parameters between the second critical point and singularity free scenarios are in fact rather subtle, [13, 145, 146]. Hence it may never be possible to rigorously confirm or deny either hypothesis.

Adding to the debate nowadays is the issue of the fragility, or lack thereof, in LDL and HDL [4, 143]. Fragility measures how rapidly the viscosity or relaxation time of a liquid varies with temperature as it approaches the glass transition, [147] - a liquid is regarded a “fragile” if its viscosity changes rapidly at the glass transition. In practice it is often not possible to measure close to the glass transition temperature, in which case the relaxation time is plotted as a function of the inverse temperature, and the extent to which this time varies according to the Arrhenius law for a strong liquid assessed [148]. The idea here is that at low enough temperatures, water undergoes an order-disorder transition, accompanied by a substantial increase in fragility. Within the realm of the hypothetical second critical point or singularity free scenarios, there is no problem with this since we are dealing with a bulk fluid, and, as was shown in the previous section, even in the stable liquid region at low temperatures there are already marked changes in water structure with increased pressure which involve much larger changes in the O-O-O angle than changes of the O-O near-neighbour distance. These changes in structure with increased pressure could be regarded as an order-disorder transition since they involve substantial bending, if not breaking of hydrogen bonds.

The idea runs into a problem however when recent claims that this order-disorder transition is observed in supercooled highly confined water are considered [68, 83, 84, 86-88, 90, 149]. Notwithstanding the experimental concerns that have already been raised about this work, if, according to theory, e.g. [146], the second critical point and associated phase diagram are shifted to lower temperatures and higher pressures by confinement, why is the fragile-strong transition apparently seen in

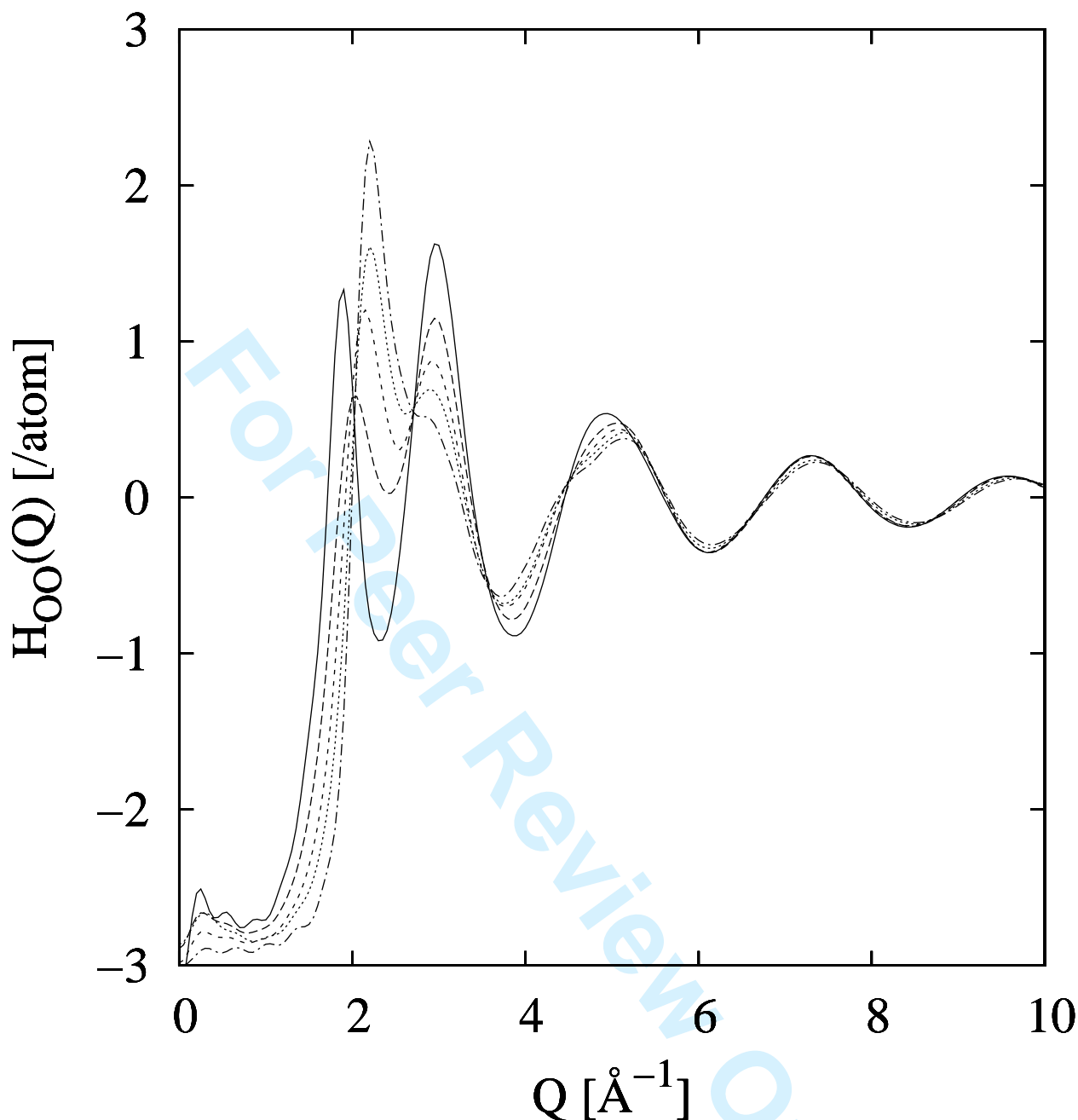


FIG. 4: The OO partial structure factors derived from the EPSR simulations shown in Fig. 3. The solid line is case (a), dashed line case (b), narrow dashed line case (c), dotted line case (d), and dot-dashed line case (e). We note that there is a marked change in the first peak positions with density, and that there are ‘isosbestic’ points - places where all the curves pass through the same value. These points arise from the linear nature of the change in the structure with density. Such points have traditionally been used to indicate that intermediate states are composed of a mixture of the two end point states, but as can be seen from the lack of low Q scattering, there is not sign of heterogeneities within the length scale of the simulations or data ($\sim 36\text{\AA}$). Hence the system remains homogeneous throughout the transition.

the confined water phase diagram under same conditions where it would be expected in the bulk water phase diagram? It would seem strange indeed that water confined to a molecular layer or two by a substrate would have a phase diagram unchanged from the bulk liquid. There

are significant issues here which are currently unresolved.

In this context it is worth revisiting the work of Jeniskens *et al.* [26–28, 150]. Using electron microscopy and electron diffraction [26] they studied thin films of water vapour deposited on an amorphous carbon film.

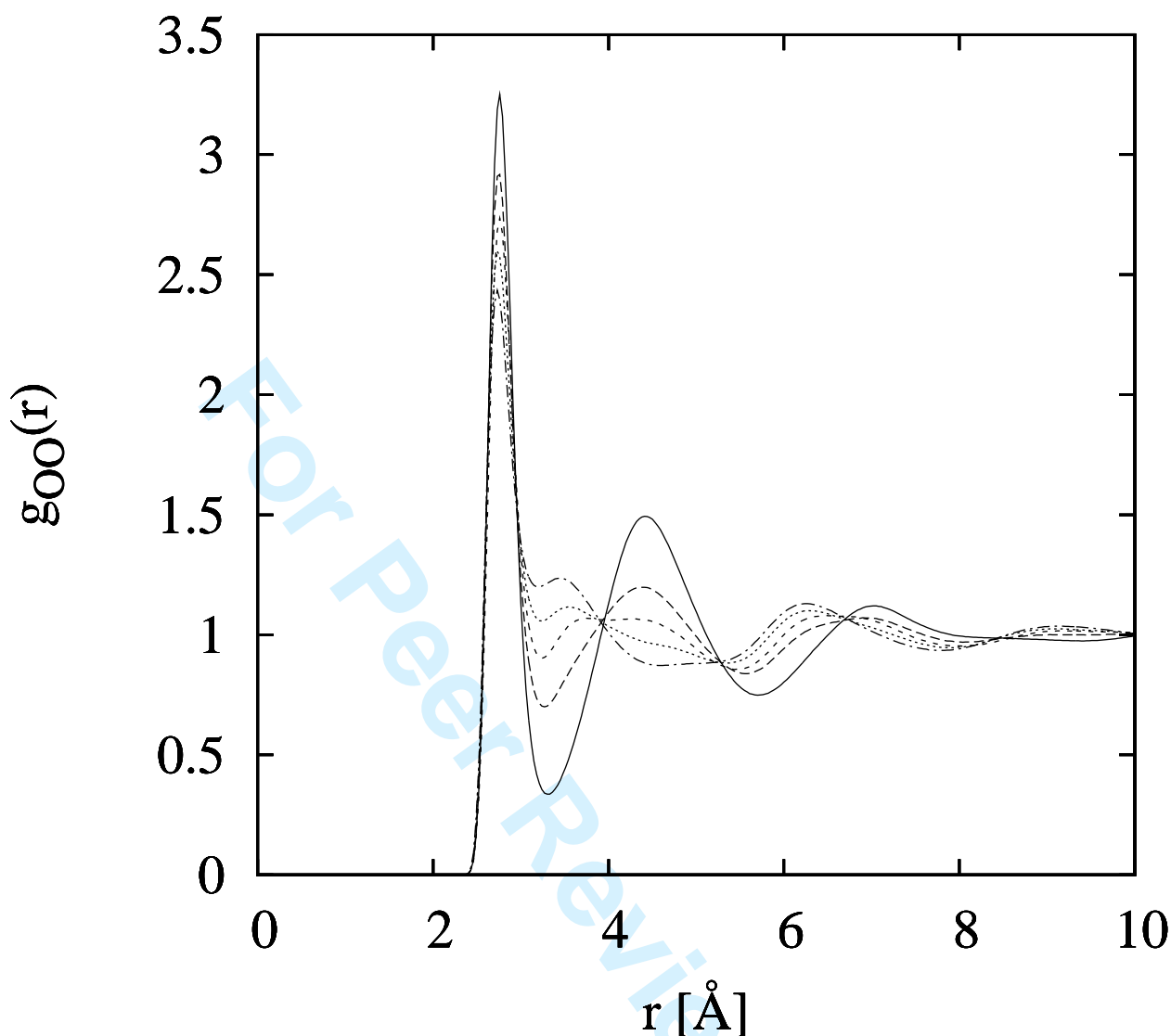


FIG. 5: The OO radial distribution functions derived from the EPSR simulations shown in Fig. 3. The solid line is case (a), dashed line case (b), narrow dashed line case (c), dotted line case (d), and dot-dashed line case (e). Note how the first peak is almost stationary with density, while the second peak first broadens, then splits, eventually taking up a much shorter distance. These trends have also been seen in computer simulations of dense water [140]

Starting from 15K they observed the (“sluggish”) transition from HDA to LDA in the temperature range 38K - 68K. Further increases in temperature cause an irreversible change in structure at about 131K, as manifested by a marked sharpening of the first diffraction peak. This was called “restrained” amorphous ice (RAI). The temperature of this change of structure varied between 122 and 136K depending on the heating rate. Crystallisation to ice Ic began occurring at 148K, but even at 175K there was evidence for significant RAI. The measurements could not be extended beyond about 180K due to the ice film subliming under the high vacuum of the experiment. Electron microscopy demonstrated [28] that above 140K this RAI was in fact a viscous liquid and per-

sisted up to at least 210K. It was described as a “strong” liquid with microcrystals of ice Ic embedded in it. Hence the conclusions here are consistent with those of Bergman and Swenson [151], but they are in disagreement with those of Smith and Kay [152], who used temperature-programmed desorption (TPD) to study the dynamics of water molecules on amorphous solid water surface. Smith *et. al.* conclude that water under these conditions is fragile.

Tanaka highlights some of the uncertainties in our understanding of supercooled, interfacial and bulk water, and argues that some of the conflicting results may be the result of experimental artifacts [153]. He proposes a conceptual two-order parameter model (TOP) which

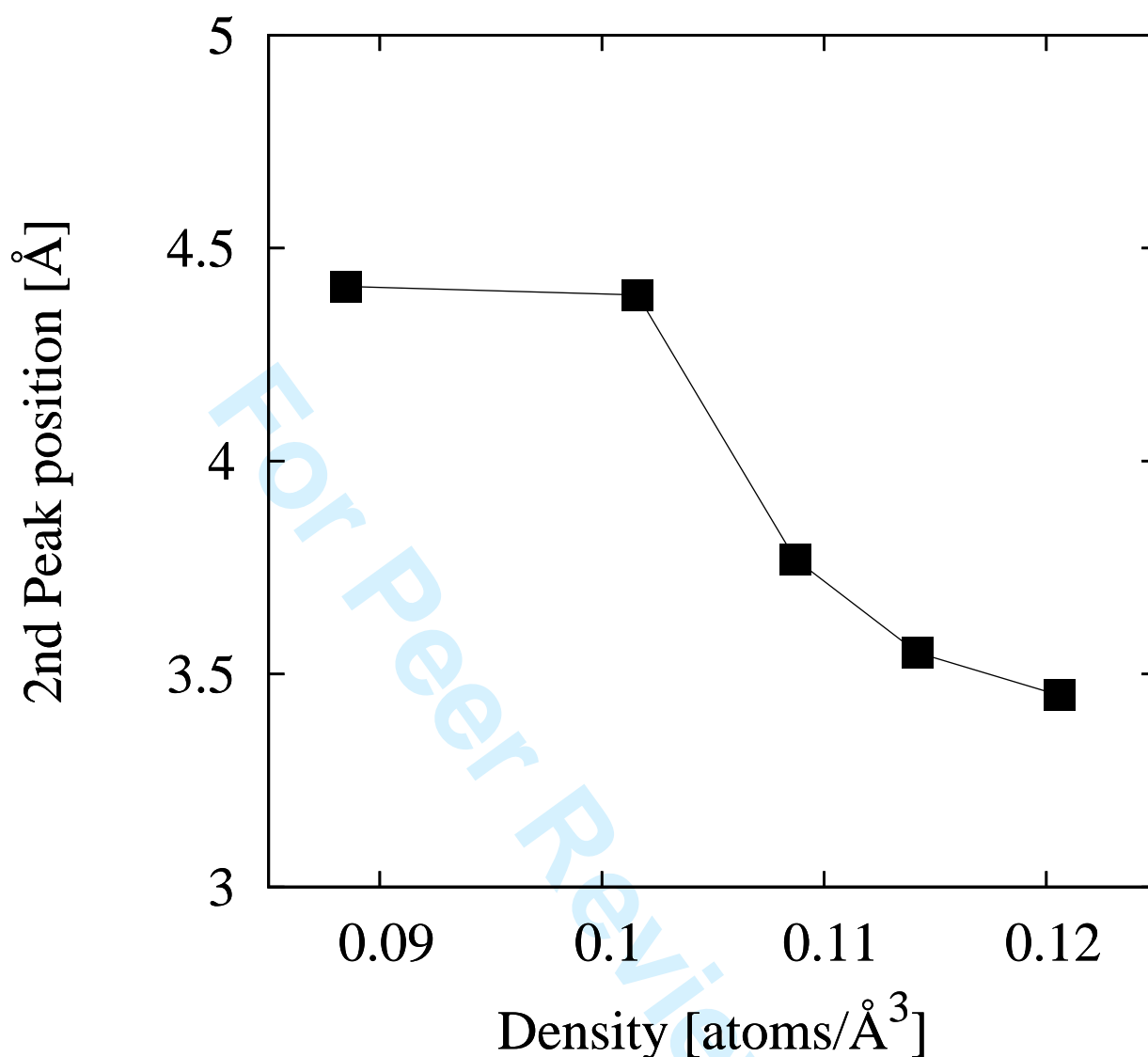


FIG. 6: Position of the second peak in the OO radial distribution functions derived from the EPSR simulations shown in Fig. 5. We see the peak position is initially constant, then changes rapidly with increasing density.

qualitatively explains the various observations. Essentially the idea is to regard water as consisting of two types of orderings, namely a density ordering driven by the isotropic part of the interaction potential, which gives rise to normal-liquid structures (NLS), and bond ordering, driven by symmetry-selective interactions, which gives rise to locally favoured structures (LFS). For water the latter would be the tetrahedron consisting of five water molecules. Note that this TOP model is distinct from a two-state model of water in that LFS and NLS continually and rapidly transform into each other. Tanaka then shows how these assumptions can be used to explain why water has a minimum melting temperature with increased pressure, as well as the fact that (a) it appears unusually fragile in the stable liquid region, but apparently strong in the highly supercooled region, (b)

it is difficult to vitrify, and (c) the viscosity of water first decreases with increase in pressure. In essence these unusual properties are to do with the interplay between the LFS and NLS as a function of temperature and pressure. This model is given a mathematical framework in later papers, see [154] and the two papers which immediately follow it, and is applicable in general to many different liquids.

Do the observed structures of HDL and LDL support the ideas of the TOP model? The bond angle distributions shown in Figure 8 certainly would indicate there is a radical change in local order between the two structures. It is questionable however whether HDL is more like a normal liquid than LDL, given that the OO radial distribution functions for either liquid do not appear “normal”, Fig. 5. In figure 9 are shown the spatial den-

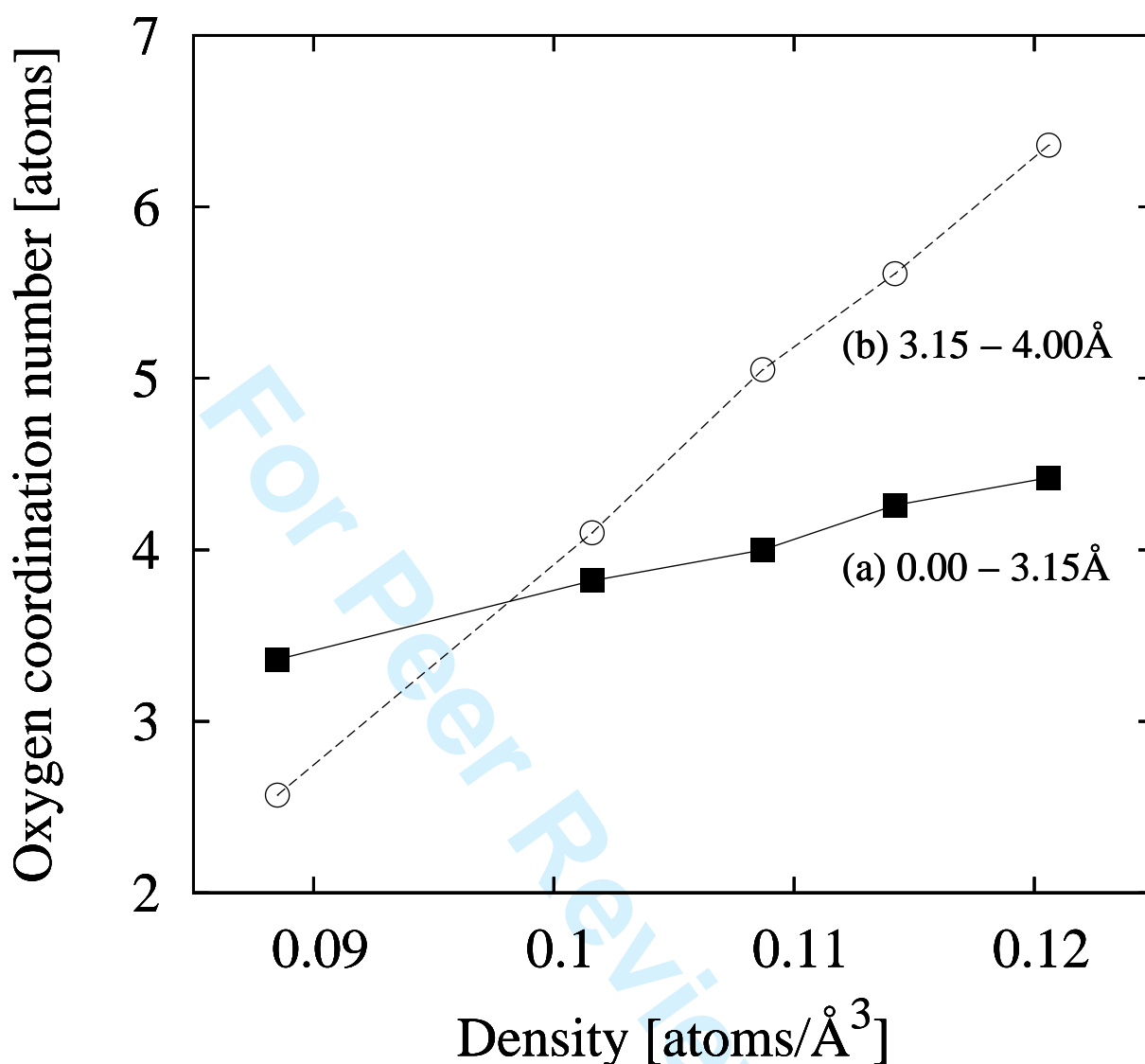


FIG. 7: Coordination number over the distance range 0 - 3.15Å (a) and 3.15 - 4.00Å (b). We note how the coordination number for the inner shell rises slower than the density change (36% for the density change compared to 32% for the first distance coordination number change). In contrast the coordination number over the second distance range grows by nearly 250%.

sity functions for LDL and HDL over two distance ranges: the first corresponds to the first 4 molecules in the coordination sphere, the second includes the first 8 water molecules in the coordination sphere. It is seen that the first 4 molecules adopt closely analogous structures in both cases, with at least 90% of the first four forming a disordered tetrahedron around the central molecule. The second shell of 4 molecules are also similar in orientational symmetry, but the main change is that the distance of this second shell has shrunk considerably in HDL compared to LDL. In HDL the second shell is almost coincident with the first. It is this change in the second shell distance that constitutes the primary difference in the two structures, and generates the markedly different bond angle distributions, Fig. 8, yet the under-

lying theme of tetrahedral local coordination is common to both liquids. This change is closely reminiscent to the structure of ice VII, where two interpenetrating hydrogen bonded networks occur which apparently do not bond to each other [155]. It would seem too simplistic therefore to describe HDL simply as a “normal” liquid structure. Note that the trends seen here are closely parallel to what was seen in the amorphous ices at much lower temperatures [112, 139, 156], so they do appear to be a common theme of water and amorphous ice, even if, as some authorities insist, water and amorphous ice are disconnected thermodynamically. Note that when attempting to rationalise the bond angle distribution functions, Fig. 8, with the spatial density functions, Fig. 9, it is important to recognise that the bond angle distribution

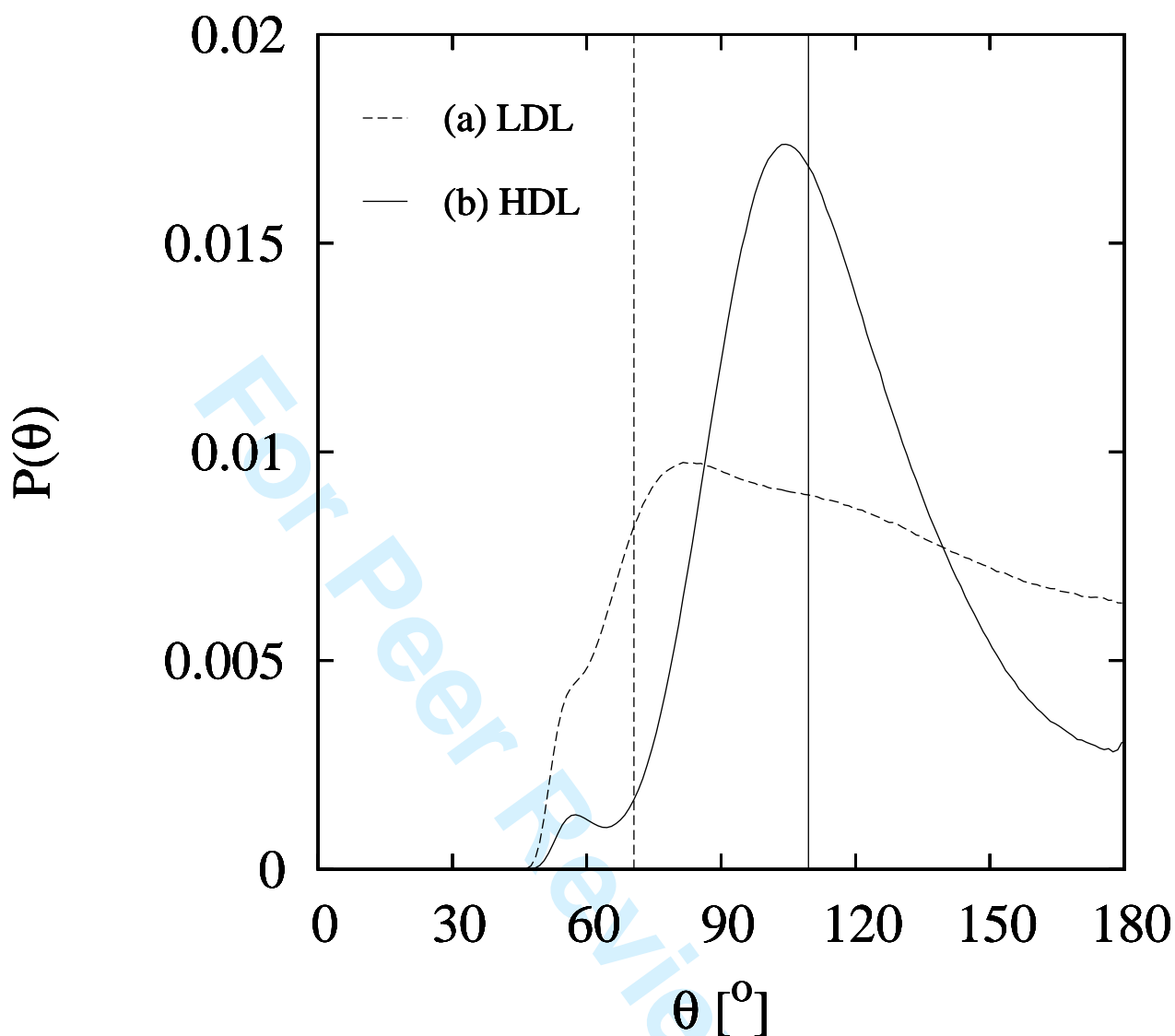


FIG. 8: O-O-O bond angle distributions for extrapolated LDL ((a), solid line) and HDL ((b) dashed line). O-O pairs are identified when they are less than 3.15\AA apart, and the distribution of included angles for triplets of oxygen atoms which satisfy this condition. The distributions have been normalised to the $\sin\theta$ dependence that would occur in a random distribution of included angles. Vertical lines are drawn to show where the peaks in this distribution would occur in an ideal tetrahedral bonding arrangement as in ice Ih (solid vertical line) and in an ideal ice VII structure (dashed and solid vertical lines).

is a three-body correlation function averaged over many triplets of water molecules, whereas the spatial density function is a pair correlation function, having integrated out all three body correlations. Hence the two functions are consistent with each other, but you cannot derive accurate three-body information from the spatial density function.

Are these structures consistent with the second critical point scenario? In the stable liquid region we clearly can have two structures that transform continuously into one another just by manipulating the pressure, and without the need to invoke heterogeneities in the local order. Both high and low density water have local tetrahedral

coordination, Fig. 9, but the angle of O-O-O triplet encounters, which for LDL is primarily tetrahedral-like, for HDL occurs over a much broader range of angles and appears to approach that found in the 8-fold coordination of ice-VII. Therefore it is this bond angle bending that characterises the change of structure between high and low density water. In the stable liquid region this bond angle distribution adjusts continuously, just as the density adjusts continuously above the liquid-vapour critical point. In the latter situation phase separation occurs, hence a critical point, when on sufficiently lowering the temperature, the attractive interactions between molecules start to compete with the repulsive interac-

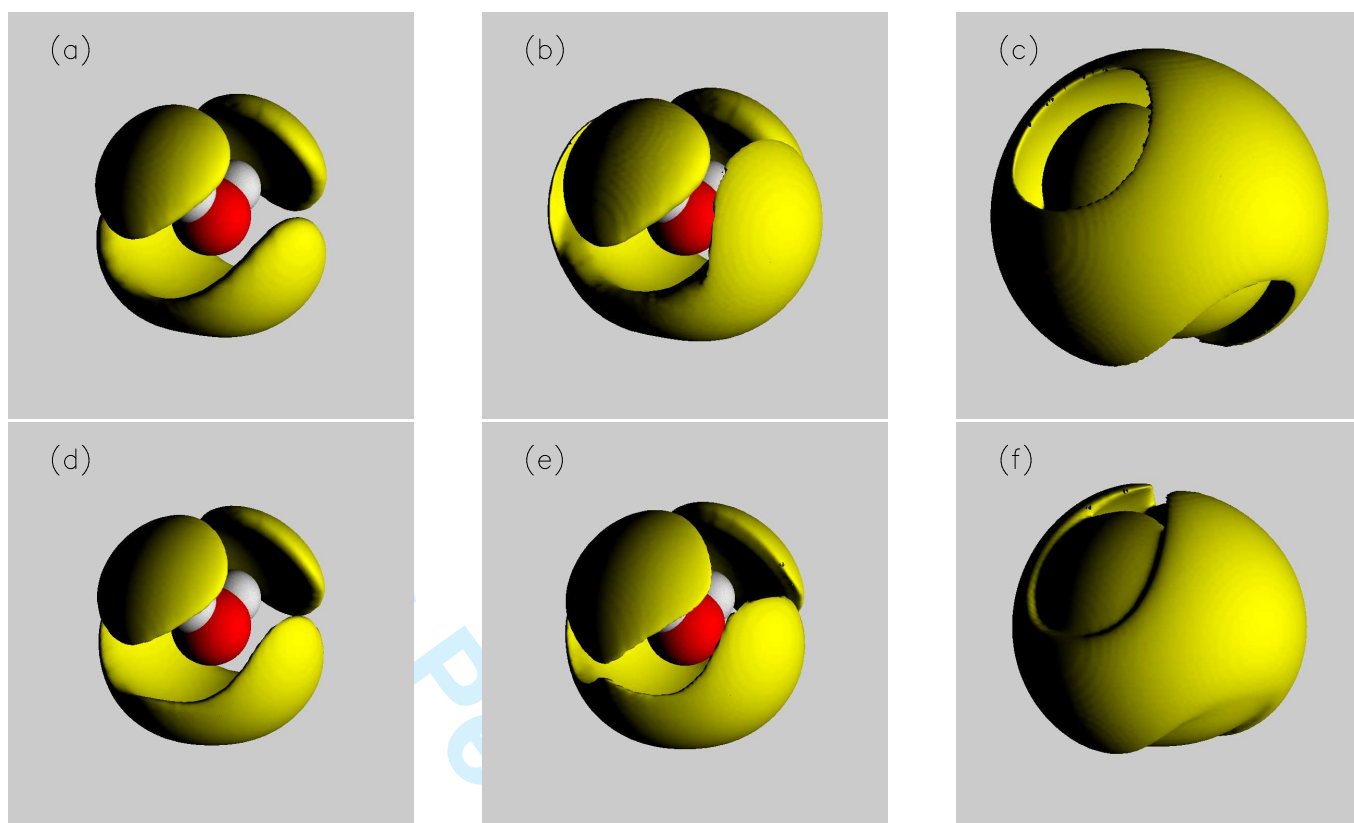


FIG. 9: Spatial density functions, $g(r, \theta, \phi)$, for low (top, (a) - (c)) and high (bottom, (d) - (f)) density water. These are shown over the distance ranges 0 - 3.55Å for (a) and (b), 0 - 3.09Å for (d) and (e), 0 - 4.24Å for (c), and 0 - 3.65Å for (f), corresponding to coordination numbers of 4 for (a),(b),(d), and (e), and 8 for (c) and (f). Contour levels are set to include 90% of the molecules in the distance range for (a) and (d), 100% of the molecules in the distance range for (b) and (e), and 80% of the molecules in the distance range for (c) and (f). We see that the inner shell of 4 molecules changes very little on compressing LDL to form HDL, remaining primarily tetrahedral in local coordination, but there is a marked shift inwards of the second shell with increased density, corresponding to the marked change in bond angle distribution, Fig. 8.

tions when molecules approach one another too closely so that two states, one more dense the other less dense, can occur with the same chemical potential at a given temperature and pressure.

It is not clear therefore that the second critical point, if it exists, derives primarily from a competition between H-bonded and non-H-bonded molecules, as is used as the basis for some models. We have seen that both high density and low density water have essentially fully tetrahedral hydrogen bonded local order on average, as do both ice Ih and ice VII. Pushing the second shell towards the first, as happens in going from LDL to HDL, or from ice Ih to ice VII, does not affect the degree of hydrogen bonding in either material very significantly. Structurally at least the likely scenario is that the O-O-O angle, or an order parameter related to it, is what allows the transition. The approach of the second shell towards the central molecule would be attractive from the point of view of the dispersion forces, but presumably repulsive as regards the fact that the central molecule is already 4-fold hydrogen-bonded. However since the approaching second shell molecule is also already H-bond saturated,

it is possible the second shell collapse could be accomplished with a relatively small change of energy, making it rather sudden at low temperatures, where the molecular motion required to keep the system under equilibrium is in any case inhibited. It should be noted that similar conclusions to the above were recently arrived at following a computer simulation study of water over a range of densities, [140].

As we have seen in the forgoing survey, this picture may be more or less correct from the structural point of view, but it does not easily explain the apparent dynamics of water at low temperature, where a number of authorities claim there is a fragile to strong transition on cooling water, but others do not agree. On the latter matter there appear to be quite disparate accounts of what is going on.

IX. SUMMARY AND CONCLUDING REMARKS

Needless to say, in a survey of this kind, with limited space and time, it is impossible to convey all aspects of the debate about the low temperature phase diagram of water. The present work has concentrated on structural aspects, to the extent that these are known from (primarily) diffraction experiments. Much of the theory, and especially computer simulation, that has gone on in the past two decades or so on this topic is not included here because it would require a completely separate and much longer review.

What is clear, irrespective of whether or not the current account covers all aspects of cold water structure, is that water is an extremely complicated substance, in spite of its molecular simplicity and symmetry. Water does not readily lend itself to study in the supercooled and amorphous states. There is a huge investment of research effort into this topic by a large group of researchers. There are theoreticians and computer simulators who try to understand the bigger picture, the underlying themes that drive water structure and properties. There are experimentalists trying to elucidate the detailed properties of particular forms of water and amorphous ice. Unfortunately the two sets of investigations don't always work well together. Inevitably experimentalists do not always agree with each other and there are a number of conflicting results, such as the whether the transformation HDA to LDA is continuous or sudden, or whether confined water undergoes a fragile to strong transition on supercooling, or whether amorphous water is thermodynamically related to ambient water. We can say with some certainty that the transition HDA to LDA if not actually discontinuous is certainly rapid and occurs over a narrow band of temperatures.

Current theoretical approaches, while having made significant advances, use terminology like fragile to strong or order-disorder transitions, which do not always make sense in the light of experimental experience. Often these terms are used by analogy with other materials rather than as accurate descriptions of what might be going on in real water. We still do not have conclusive evidence that water has a second critical point, attractive though that proposition might seem. It seems that so often in

justifying a particular theoretical claim, use is made of particular experimental results which support the proposed contention, while other data which do not support it or question it are not referred to. A lot of water theory relies heavily on computer simulation evidence, but since there is no real consensus on what is the correct interaction potential for water, different simulations often give rather different behaviours. If we are not careful we run the serious risk of making assertions based on models, intuition and hope, rather than conclusive scientific evidence.

It should also be clear from the foregoing account that we do NOT have all the evidence, or at least the available evidence is not sufficiently consistent or reproducible for us to be able to rigorously justify some of the claims that are made. We seriously need to find out what is happening to water in confined geometry, to understand how different experiments can give such widely different interpretations. This is fundamentally important to many different fields, particularly the behaviour of water in the Earth's crust, the atmosphere, and in biological organisms, where in strong confinement it affects every one of us. While we cannot observe water in the bulk at low temperatures because of the freezing that occurs, we certainly can observe the liquid at surfaces and in small droplets down to temperatures as low as 130K. Hence there is a strong drive to understand both the bulk liquid and the interfacial liquid at low temperatures.

Water in the bulk is already complicated, but at surfaces and in confinement the complications multiply in number many times because the presence of impurities and the nature of the surface topography can have a profound impact on what is observed. One has the sense that the field of interfacial water research is very much in its infancy, and has a long way to go before it is anywhere near to being fully understood.

Acknowledgments

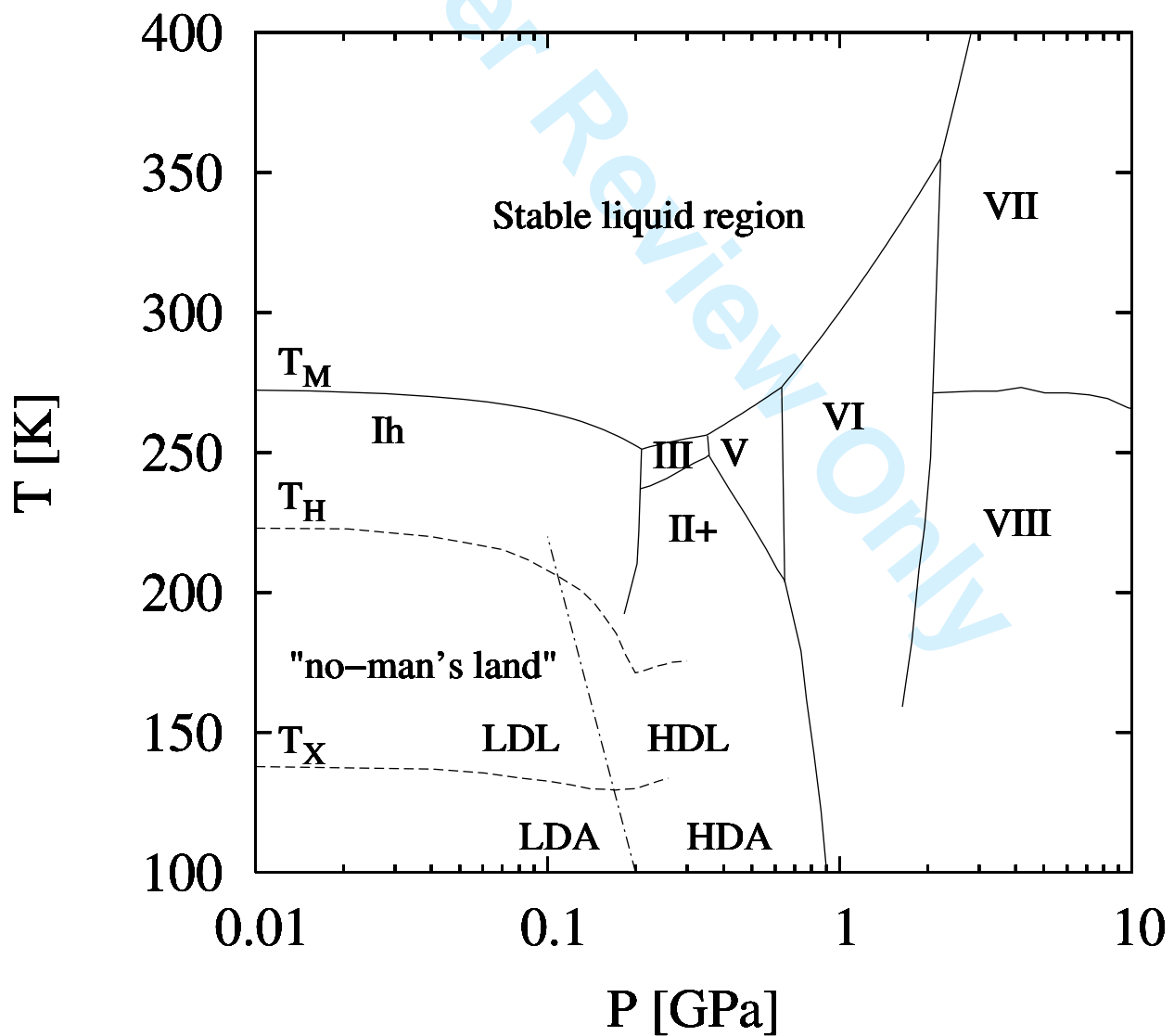
I am indebted to C A Angell for some very helpful notes and comments on the nature of the proposed order-disorder transition in cold water, and to P Debenedetti for an explanation of the Truskett *et al.* model.

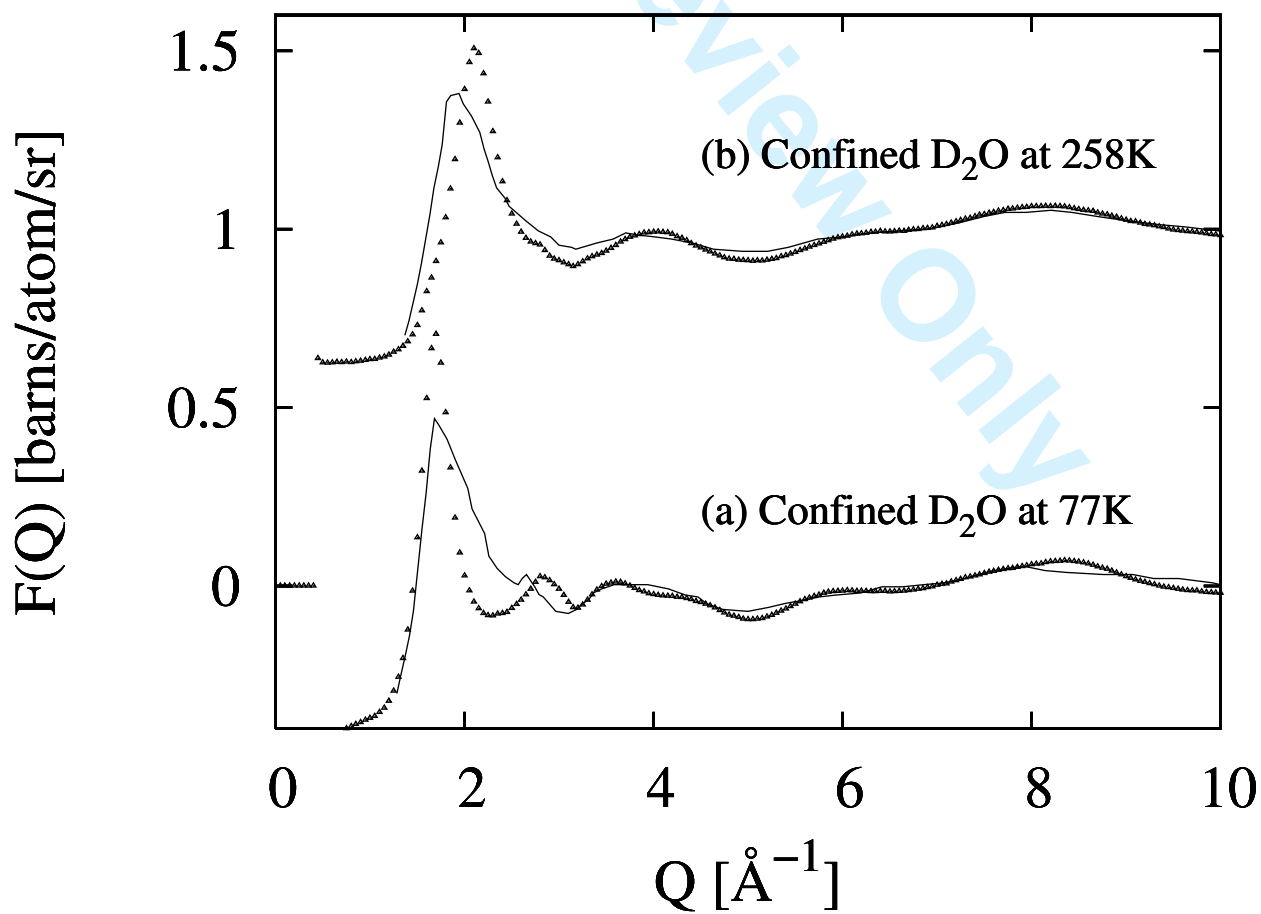
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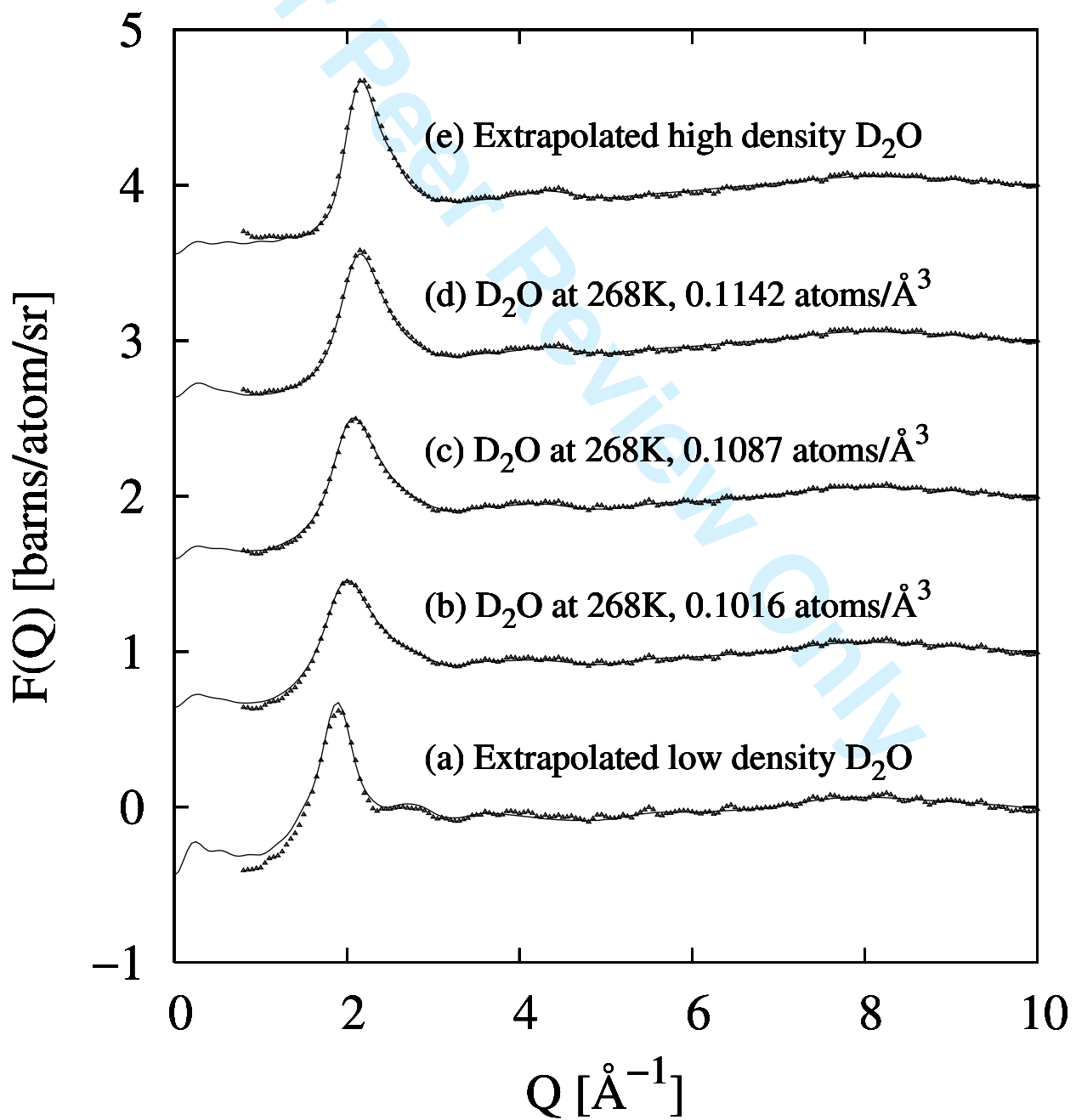
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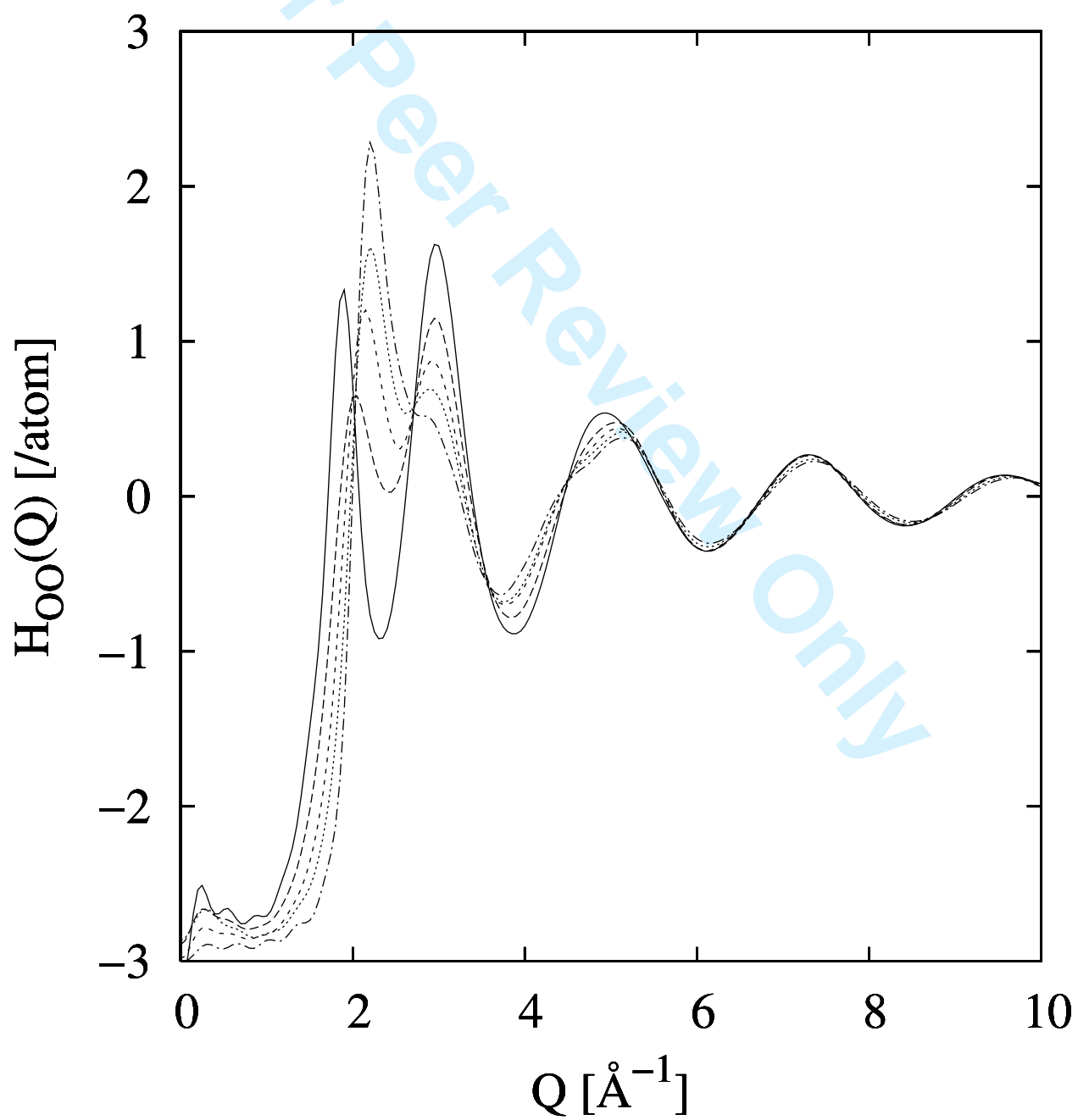
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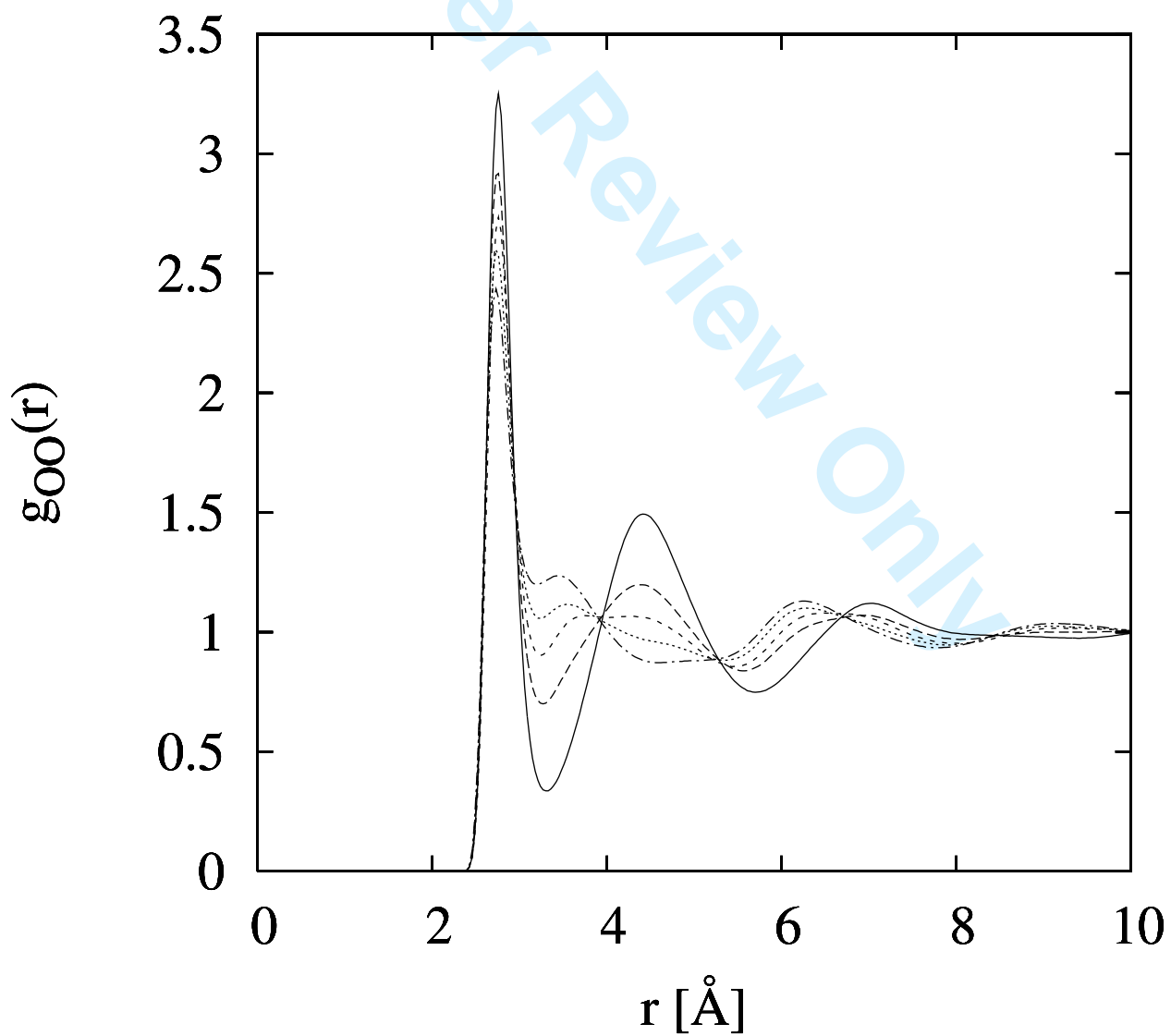
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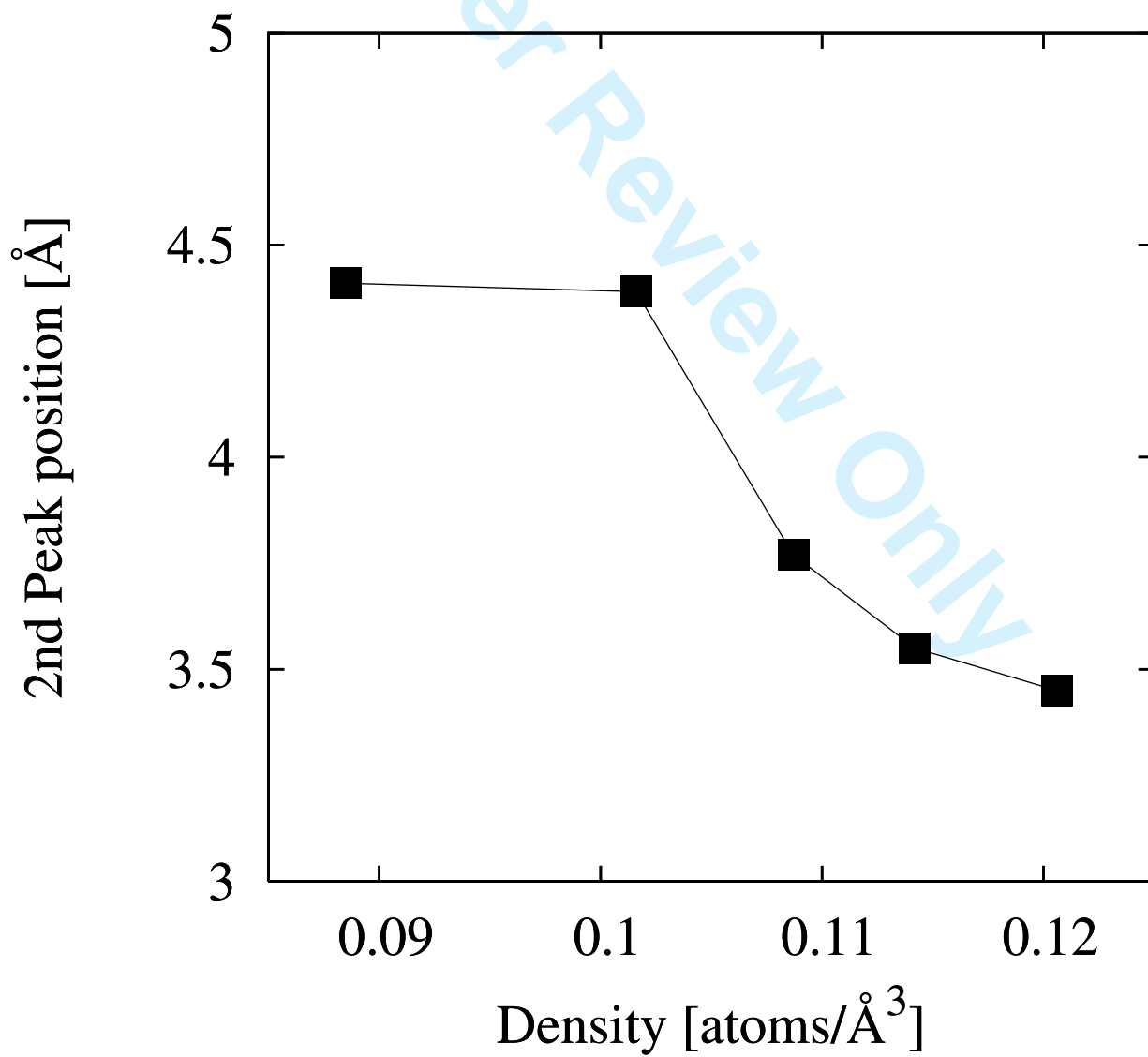


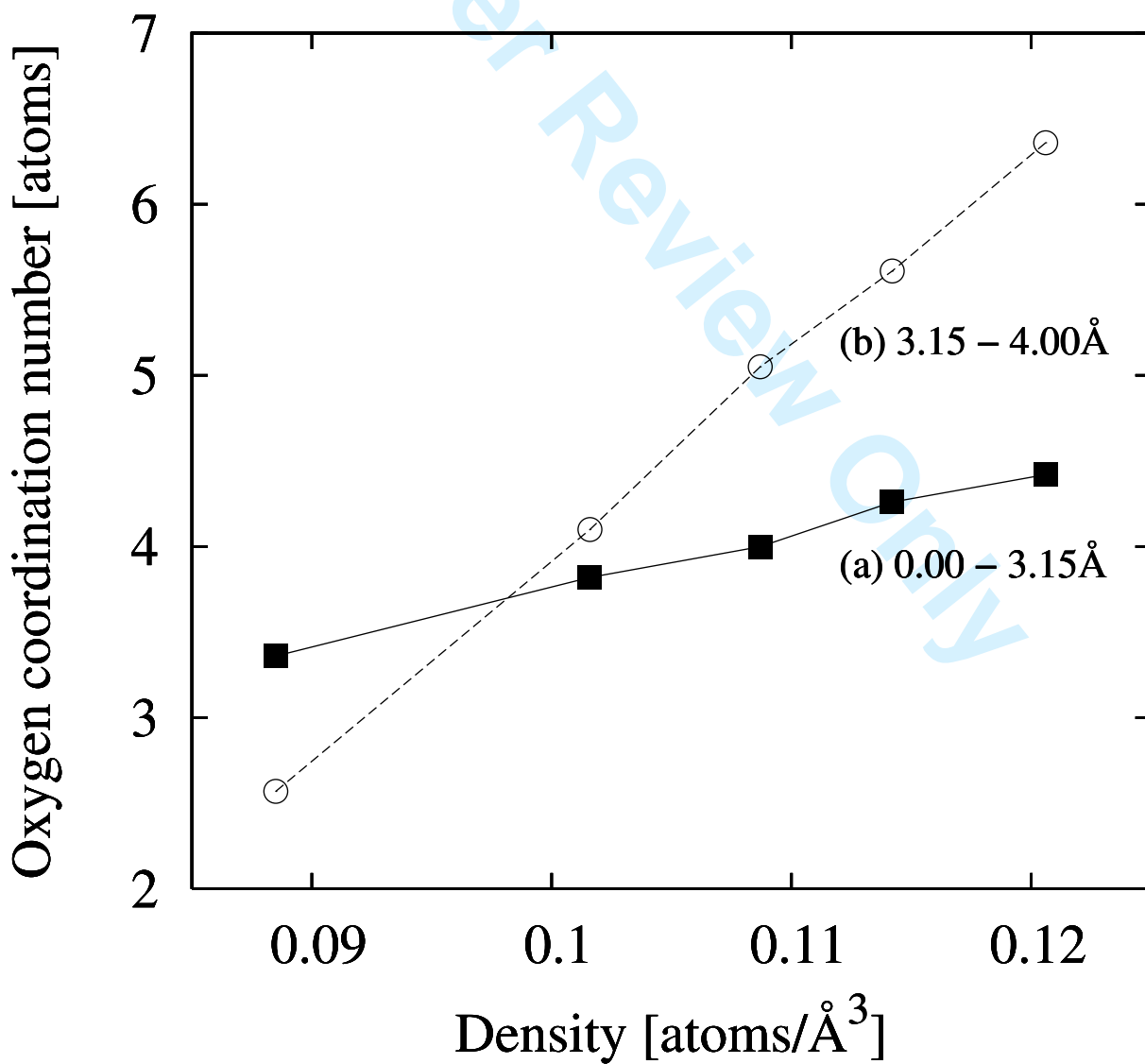


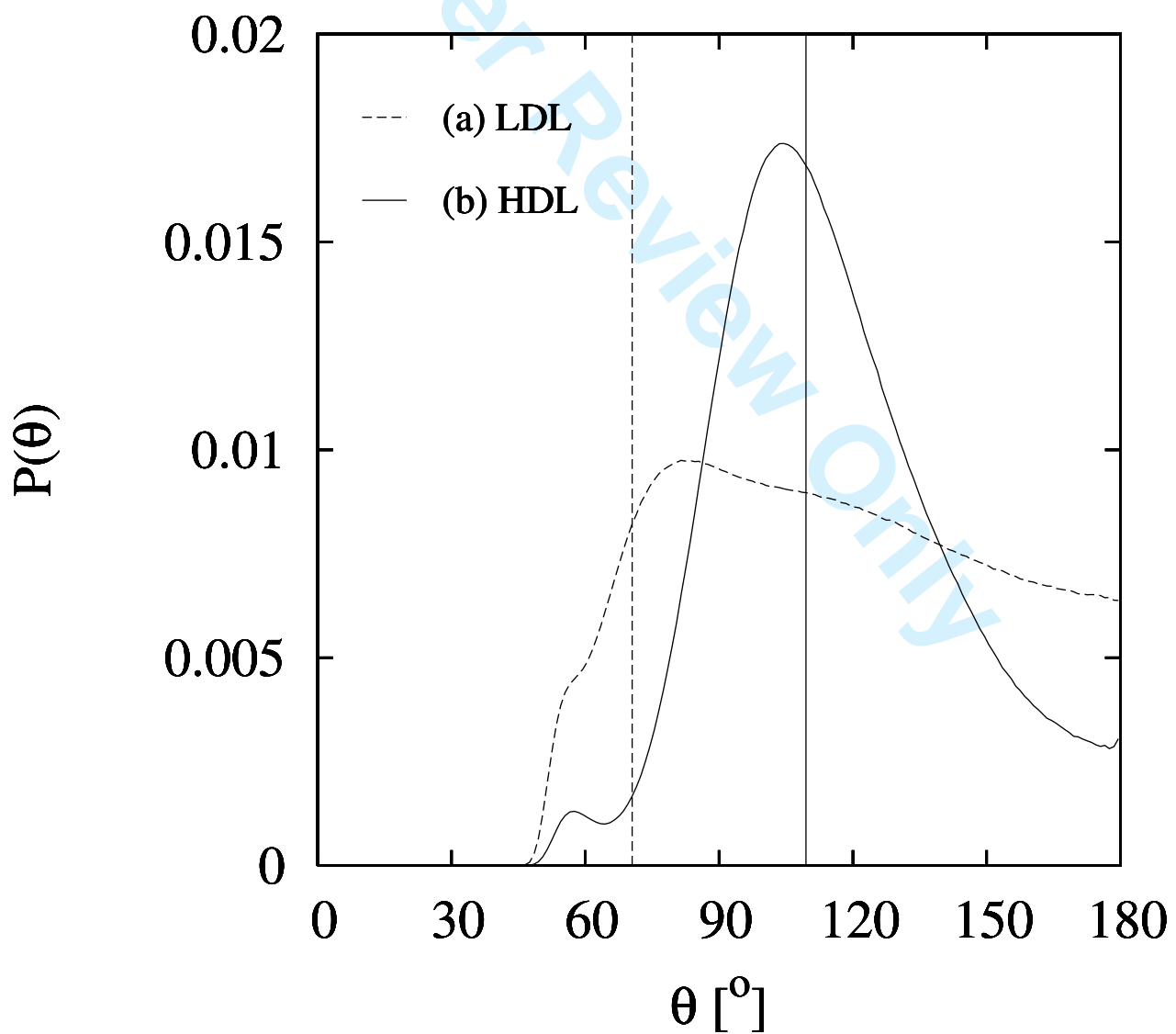




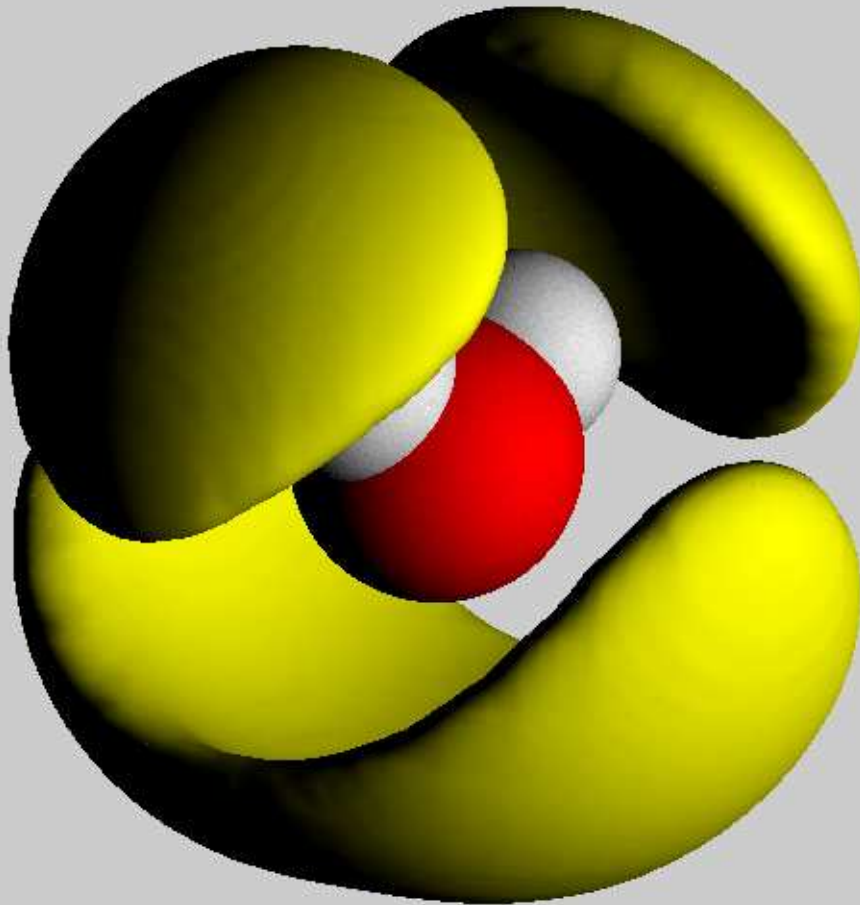








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