Neutron diffraction of hydrogenous materials: Measuring incoherent and coherent intensities separately

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Accurate determination of the coherent static structure factor of any disordered material containing substantial amounts of proton nuclei has proven to be rather problematic by neutron diffraction, due to the large incoherent cross section of ^{1}H. This problem has continued to set severe obstacles to the reliable determination of liquid structures of hydrogenous materials up to this day, by introducing large uncertainties whenever a sample with a ^{1}H content larger than about 20% had to be investigated by neutron diffraction. Huge theoretical efforts over the past 40 years which were aimed at estimating the incoherent background of such data did not result in any practical solution to the problem. Here, we present data for the coherent and incoherent contributions to the total static structure of mixtures of light and heavy water. The measurements were done using the polarized neutron diffraction technique, which uniquely allows determination of the two contributions separately. The data covers a wide range of momentum transfer (0.8–21 Å^{-1}) and the entire composition range, i.e., light water contents between 0 and 100% at five different values. We show that the measured incoherent scattering can be approximated by a Gaussian function. The separately measured coherent intensities exhibit signs of small inelastic contributions. Out of several possible approaches, we have chosen to subtract a cubic background using the reverse Monte Carlo algorithm. This algorithm has the advantage of requiring an actual physical model with thousands of realistic water molecules at the correct density describing the corrected data. Finally, coherent static structure factors for five different compositions of liquid H_2O and D_2O mixtures are presented for which the huge incoherent background could actually be measured and separated, instead of being approximated as it has been done so far. These experimental results provide a strong hope that determining the structure of hydrogenous materials, including, e.g., protein solutions, may become feasible in the near future.

I. INTRODUCTION

Trustworthy information concerning the microscopic structure of liquid water, the best known hydrogenous material, is essential for most physicists, chemists, geochemists, and biologists, simply because life on Earth is based on water. For this reason, liquid water has been the subject of a large number of diffraction studies (see, e.g., Refs. [1–4]). Computer simulation investigations using classical (for a review, see e.g. Ref. [3]) and quantum-mechanical (see, e.g., Refs. [5] and [6]) force fields abound. A key point here is that the development of force fields is biased by experimental results; this is also a reason why reliable diffraction data are indispensable.

Despite voluminous relevant literature, liquid water is still viewed as one of the most notorious puzzles: for instance, there are open questions concerning the average number of hydrogen bonds per molecule [6,7]. It is also sometimes argued that an uncertainty exists regarding even the position of the first intermolecular O-H distance—a crucial one, as it characterizes hydrogen bonding [8]. The reason why these questions are still open is, quite clearly, the presence of *hydrogen*.

X-ray diffraction is only a little sensitive to hydrogen and can provide information only on oxygen-related pair correlations. In neutron diffraction, separating the three partial contributions would be possible via the contrast variation between ^{1}H and ^{2}H ("H/D isotopic substitution") [1,2]. This, in principle, allows us to derive the most detailed information on the microscopic structure of hydrogenous (i.e., containing ^{1}H) systems, due to the nice contrast between their coher-

ent neutron-scattering lengths [9] ($b_c^H = -3.740\,6$ fm and $b_c^D = 6.671$ fm).

In neutron diffraction the structure factor of ^{1}H$_2$O is the one with the highest information content, for the negative coherent scattering length of ^{1}H: negative peaks would signify characteristic O-H distances in the total radial distribution function. However, as neutrons possess a $(+/-)$ 1/2 spin, the scattering of unpolarized neutrons on nonzero nuclear spins results in a "spin-incoherent" scattering, whose cross section is exceptionally high for ^{1}H ($\sigma_i^H = 80.27$ b and $\sigma_i^D = 2.05$ b). Thus the measurable neutron diffraction signal from pure ^{1}H$_2$O is overwhelmed by incoherent scattering that is useless from a structural point of view (see, e.g., Ref. [1]). As a consequence, the structure factor of ^{1}H$_2$O is still much debated [1,2,8], because even small errors in it have a large impact on the O-H partial radial distribution function.

Reliable neutron total structure factors of water samples with high light water content (ideally, of pure ^{1}H$_2$O) would be decisive concerning H-bonding in water. For this reason, numerous suggestions over the past 40 years have been made for the treatment of the huge "incoherent background" (for an informative figure, see, e.g., [1]), none of which has proven to be routinely applicable. (For the various approaches, see Refs. [10–15].) Real improvement could be expected only from an accurate experimental determination of the incoherent contributions from ^{1}H over the relevant momentum transfer range; this, unfortunately, has proven to be impossible thus far.

Spin incoherence can, in principle, be tackled by separating the coherent and incoherent parts of the measured diffraction signal; this can be realised by using polarized neutrons (see, e.g., Ref. [16]). By measuring total scattering intensities as recorded by "non-spin-flip" (NSF) and by "spin-flip" (SF) modes of the instrument, the coherent and spin-incoherent intensities can be extracted using the following formulas:

$$I_{\text{coh}}(Q) = I^{NSF}(Q) - \tfrac{1}{2}I^{SF}(Q) \qquad (1)$$

and

$$I_{\text{incoh}}(Q) = \tfrac{3}{2}I^{SF}(Q). \qquad (2)$$

Interestingly, potentialities of polarized neutron diffraction have only been little exploited in this field. A possible reason for this is that available instruments provide data over only narrow momentum transfer ranges, so that traditional evaluation, involving direct Fourier transformation, would not be applicable. Concerning liquid water, only a couple of such investigations have appeared [17,18], without any significant practical use.

II. EXPERIMENT

Diffraction experiments using polarized neutrons have been conducted on the D3 instrument [19] installed on the hot source of the Institut Laue-Langevin (ILL; Grenoble, France). Five isotopic compositions of ^{1}H (protons) and ^{2}H (deuterons) have been prepared, containing 0, 20, 40, 64 ("zero water," see, e.g., [18]), and 100% light water (with ^{1}H). Liquid samples were put in a double-walled vanadium container (internal diameter 8 mm, outer diameter 10.7 mm) in order to minimize contributions from multiple scattering; the sample geometry was therefore that of a hollow cylinder. The experiments were performed at ambient pressure and temperature. Using the D3 instrument with 0.5 Å wavelength neutrons, scattering intensities were collected in both spin-flip and non-spin-flip modes over a uniquely wide momentum transfer range of 0.8–21 Å^{-1} (4–120 deg in 2Θ). The hot neutron source of the Institut Laue-Langevin can provide a high flux of such short-wavelength neutrons, which is the prerequisite for studies like reported here. This outstanding coverage of the reciprocal space can be realized by making use of a Heussler-alloy polarizer and a ^{3}He analyzer cell that contains spin-polarized nuclei [20]. We emphasize that, although it has not been designed for liquid diffraction, the D3 instrument at present is the only one in the world where studies of this kind may be conducted.

Samples with the highest ^{1}H content have been investigated for somewhat longer time than those dominantly with ^{2}H, so that statistics of the coherent signals would be comparable. Still, the measuring time of about 24 h for pure light water provided statistics somewhat poorer than hoped for. The usual corrections [21] for polarization efficiency have also been carried out before further data processing. Coherent and spin-incoherent contributions to the total scattering have been separated in the usual manner [16] by Eqs. (1) and (2).

III. RESULTS AND DISCUSSION

A. Incoherent scattering

Figure 1 shows the incoherent intensities, which are directly proportional to the spin-incoherent cross sections, up to 21 Å^{-1}.

Following a couple of trial attempts, it has become clear that a single Gaussian and an additional constant are perfect for fitting the measured signals within errors (see Fig. 1). Note that this functional form, that has not been suggested explicitly by any of the corresponding studies of the incoherent background [10–15], operates with only three adjustable parameters: *intensity*, *FWHM,* and a *constant*. These are listed in Table I for the five mixtures of light and heavy water considered in this study. Furthermore, the similarity of the Gaussian width parameters obtained for the individual measurements suggested that a fit using a *common (identical) width* parameter for all measurements might be applicable.
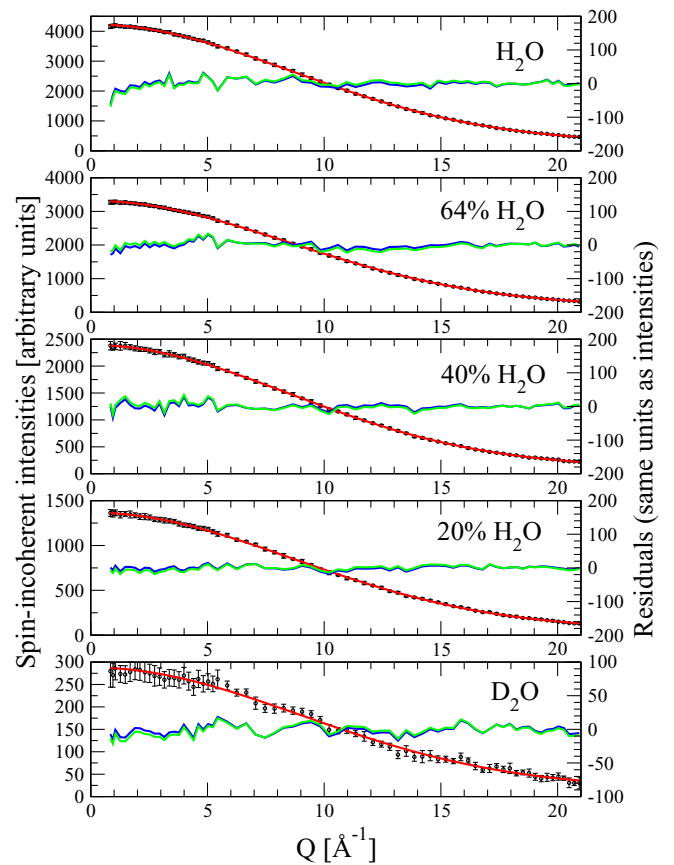

FIG. 1. (Color online) Incoherent intensities, obtained by multiplying the measured "spin-flip" intensities by 3/2 [see Eq. (2)] for five mixtures of light and heavy water. Light water content (from top to bottom): 100%, 64%, 40%, 20%, and 0%. Symbols with error bars: measurement; red solid lines: Gaussian (plus constant) fits; blue solid lines: residuals; green solid lines: residuals from the fit with a Gaussian of identical width. The statistical accuracy deteriorates as light water content decreases. This is just the manifestation of the well-known fact that pure heavy water (containing only ^{2}H nuclei of the element hydrogen) shows only a small amount of spin-incoherent scattering. This is why neutron diffraction is most frequently performed on deuterated samples.

TABLE I. Adjusted parameter intensity, FWHM, and constant term, together with goodness-of-fit (R_{wp}) values while fitting the measured incoherent intensities with individual and with common FWHM [20.128(25) Å^{-1}] parameters. (The number of degrees of freedom was 68 for each individual fit and 344 for the common FWHM fit during the actual calculations.)

^1H_2O content [%]	Individual fits				Fit with common FWHM		
	Intensity	FWHM [Å^{-1}]	Constant term	R_{wp} [%]	Intensity	Constant term	R_{wp} [%]
100	85550(163)	20.217(31)	258.8(2.9)	0.53	85140(166)	266.7(2.7)	0.56
64	66752(120)	19.974(30)	175.0(2.1)	0.58	67267(135)	165.7(2.12)	0.68
40	48414(114)	19.955(40)	111.8(2.2)	0.77	48814(113)	102.8(1.8)	0.87
20	28323(102)	20.381(61)	61.6(2.1)	1.08	27980(68)	69.5(1.16)	1.21
0	6093(146)	21.193(385)	17.8(3.2)	4.75	5746(45)	25.8(0.88)	5.04

The identical width of FWHM = 20.128(25) Å^{-1} provided only slightly worse goodness-of-fit (R_{wp}, as defined in [22]) values than the individual parametrization, so that agreements between fits and original curves are still good. The residuals are also shown in Fig. 1; differences between fits and measured curves are exclusively of statistical nature.

A short comment may be in order here: it is not yet clear whether the parameters of the Gaussian functions (i.e., the exact shape of the incoherent contribution) depend on the wavelength of the neutron beam. Since this is an important issue from the point of view of the transferability of the results presented here, we plan to perform control experiments using polarized neutron beams with different wavelengths.

B. Coherent scattering

In Fig. 2, coherent intensities, as derived from a simple linear combination of the separately measured "spin-flip" and "non-spin-flip" intensities, are displayed. Although the statistical accuracy may be further improved for the mixtures with the highest ^1H content, it is obvious that the functions are free from the enormous spin-incoherent background (cf. [1,23]). What is left to handle is a gentle droop towards higher Q-values that is characteristic of inelastic effects. Numerous approximations have been suggested to correct for such backgrounds, starting from the pioneering work of Placzek [24] (which, as the author himself warned, is not appropriate for hydrogen), to modern numerical fitting algorithms (see, e.g., [25–29]).

For our present purposes, the reverse Monte Carlo (RMC) method of structural modeling [29,30] has been selected. The main reason for this choice was that in RMC, thousands of realistic molecules have to be present at the correct density in physically existing simulation boxes; that is, the limiting values of the radial distribution functions and structure factors are automatically built in. A cubic background may also be refined simultaneously with the usual approach to the measured data via random moves of the particles.

During the modeling, the calculations were performed with 2000 molecules using an atomic number density of 0.100 28 Å^{-3}. The H_2O unit was kept together by using fixed neighbor constraints [29], allowing small variances of the interatomic OH (0.98 ± 0.02 Å) and HH (1.55 ± 0.03 Å) distances. Between atoms belonging to different molecules, closest approach distances were applied (OO 2.2 Å, OH 1.5 Å, HH 1.6 Å).

Results from such RMC calculations are presented in Fig. 3, in the form of normalized coherent static structure factors. Again, it may be argued that, statistically, measured curves for the mixtures with the highest ^1H contents are not as good as the ones that correspond to the ^2H-dominated samples; still, corrections for inelasticity could also be performed successfully. That is, the measurement-based determination of the spin-incoherent background for hydrogenous samples has directly led to coherent static structure factors, a result that has been awaited for decades.
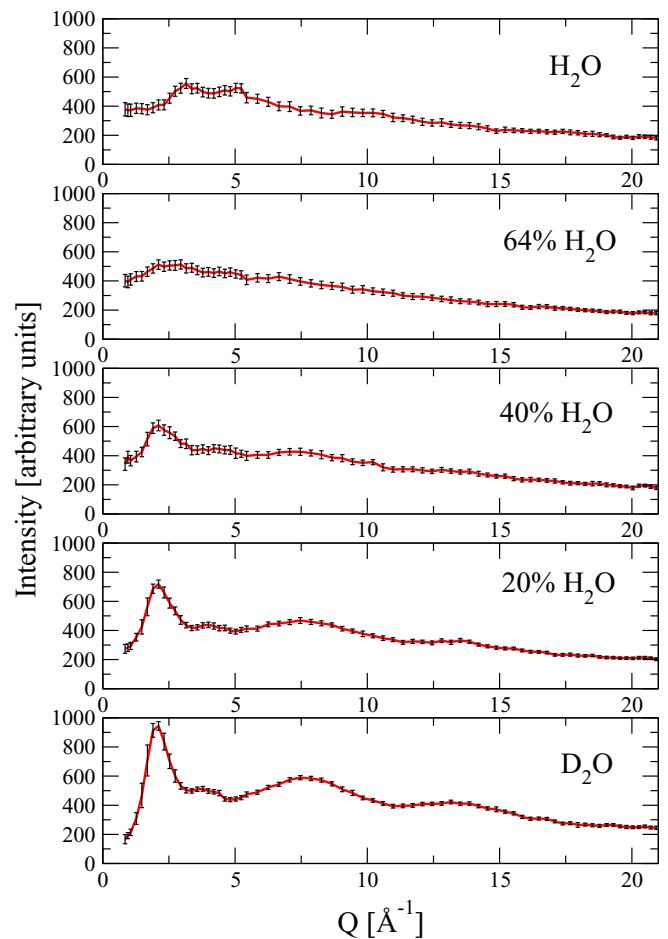

FIG. 2. (Color online) Coherent intensities obtained via Eq. (1) for five mixtures of light and heavy water. Light water content (from top to bottom): 100%, 64%, 40%, 20%, and 0%.
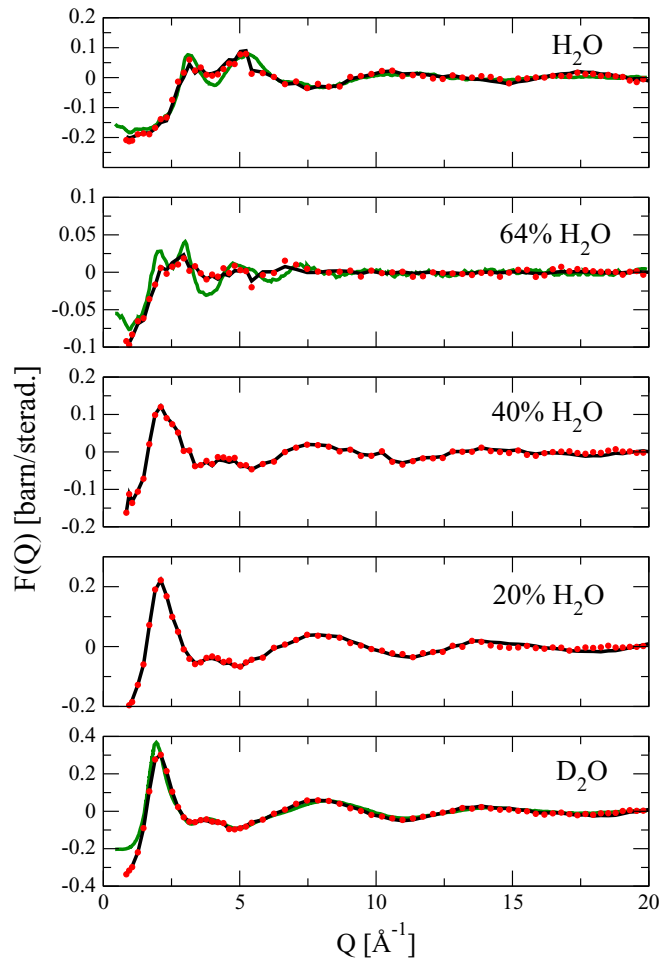
FIG. 3. (Color online) Coherent static structure factors for five mixtures of light and heavy water. Light water content (from top to bottom): 100%, 64%, 40%, 20%, and 0%. Red dots: experimental points; black solid lines: reverse Monte Carlo fits. For three compositions, also shown are the latest results from nonpolarized neutron diffraction [31] (green solid lines). Deviations between directly measured (red dots; present study) and approximated (green solid lines; Ref. [31]) are considerable.

In Fig. 3, very recent total scattering structure factors (TSSF) derived from nonpolarized neutron diffraction [31] are also shown (only for pure light and heavy water, and "zero water"). First of all, the low-Q behavior of the nonpolarized data would certainly need attention. At higher Q, above about 1.5 Å^{-1}, polarized and nonpolarized results are within acceptable error margins only for pure heavy water, although the discrepancy around the first maximum might warrant further investigations. Differences between TSSF values of samples with high ^{1}H content raise serious concerns, particularly for the case of "zero" water, and necessitate detailed further investigations concerning data processing on one hand, and issues with statistics on the other. As a followup, even (RMC and empirical potential structure refinement, EPSR (see Ref. [2])) structural modeling will have a task to complete: it will have to be made clear whether the deviations between polarized and nonpolarized neutron diffraction data are reflected in the actual structural models of liquid water.

For a demonstration of the robustness of our approach, in Fig. 4 the separated coherent and incoherent intensities are displayed, together with their sums; the sums represent the information measurable by standard (i.e., nonpolarized) neutron diffraction. Note that even in the case of pure heavy water, the precise knowledge of the incoherent intensity is desirable. For samples with more than (about) 20% ^{1}H content, the incoherent contributions are much greater than the coherent ones and therefore, proper handling of them is only possible if one can measure both contributions separately.

Before concluding, it is appropriate to remember that there are still inherent (although, in comparison with the problem of spin incoherency, subtle) difficulties with the particular case of liquid water (for a useful review, see, e.g., Ref. [32]). First of all, pure light and heavy water display detectable thermodynamic differences when they are at the same temperature that may influence the results of diffraction measurements too (see, e.g., Ref. [33]); also, for the large difference between the coherent scattering lengths of the proton and the deuteron, the level of isotope incoherence is also of concern. These problems are not specific to the approach proposed here: they have been present in all structure studies of liquid water. Now, after the major difficulty could be overcome, more attention may be devoted to the remaining smaller issues.

IV. CONCLUSION

Summarizing the achievements reported here: (1) the incoherent and coherent scattered intensities from hydrogenous water samples, including pure light water, have been determined by polarized neutron diffraction over an unprecedentedly wide momentum transfer range; (2) the incoherent intensities could be described, within statistical error, by Gaussian curves and a constant using three adjustable parameters only, a finding which may later be used for correcting data from nonpolarized neutron diffraction; (3) the separated coherent intensities are shown to contain roughly equal proportions of inelastic contributions, which is consistent with the notion that their origin lies in molecular recoil effects (as opposed to single-atom relaxation); (4) this remaining inelastic background could easily be corrected for by using the RMC method of structural modeling, thus providing the coherent static factors for hydrogenous materials with an arbitrary amount of protons ^{1}H; significant differences between "traditional" [31] and polarized neutron diffraction results have been revealed that need further, close attention.

There may be far-reaching consequences of the present findings: (1) it has now been demonstrated that hydrogenous samples without deuteration can be handled by (polarized) neutron diffraction, which, in turn, means that the microscopic structure of "soft matter" systems of any complexity (like, for instance, reported in Refs. [34] and [35]) can be considered; (2) the H/D isotopic substitution, wherever feasible, may now gain an enhanced reputation, since the large contrast between the coherent scattering lengths of ^{1}H and ^{2}H may be fully exploited; (3) it is now clear that for a proper consideration of incoherent contributions from hydrogenous samples, one needs to measure them at least up to Q values as reported here and the angular range should be as high as possible, otherwise the points of inflection (between 10 and 15 Å^{-1},
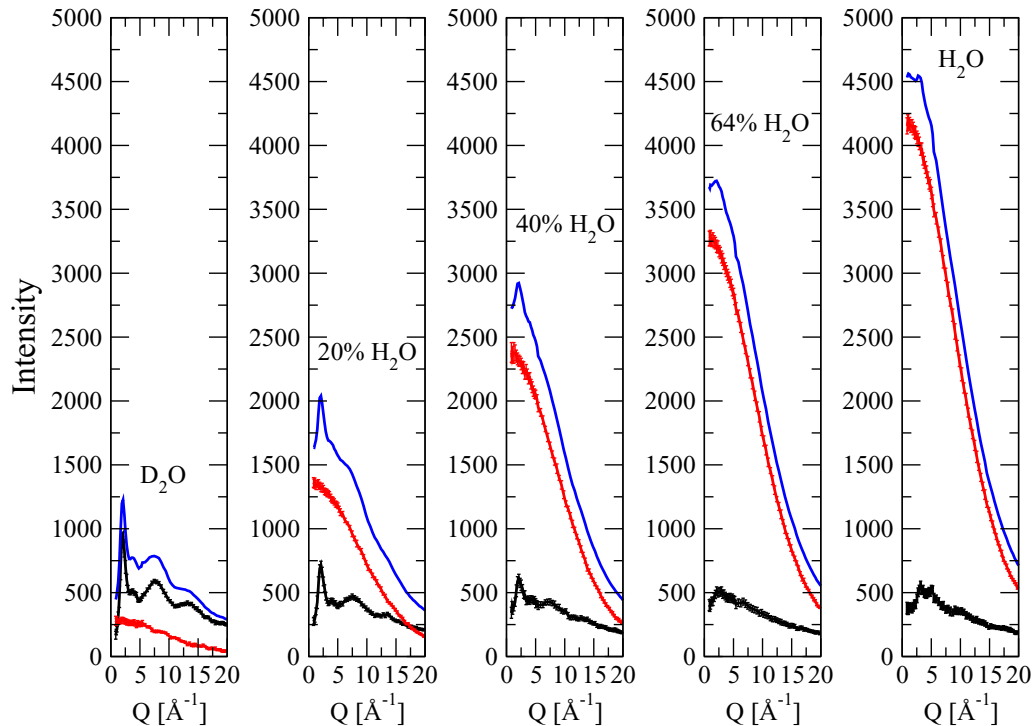
FIG. 4. (Color online) Measured spin-incoherent (red lines) and coherent (black lines) intensities for five mixtures of light and heavy water. Light water content (from left to right): 0%, 20%, 40%, 64%, and 100%. Blue lines: sums of the (here, separately measured) coherent and incoherent intensities, which therefore represent the neutron diffraction signal measurable without polarization analysis. If one wishes to reach the coherent intensities (black curves) from nonpolarized data, then a large number must be approximated (individual points of the red curves) and subtracted from another large number (individual points of the blue curves) and the desired result is a small number (individual points of the black curves). That is, taking the standard (nonpolarized) way, the statistical errors on their own are large enough to render the entire analysis problematic, not to mention systematic uncertainties in conjunction with estimating the (spin-)incoherent contributions.

see Fig. 1) will be missed; (4) since this takes extra long experiments (ideally, as we see it now, of the order of several days on the D3 instrument for just one hydrogenous sample with ^{1}H only), a very carefully planned list of the "reference" samples, to be measured by any means, has to be drawn; (5) we envisage an inevitable boost in developing polarized neutron instrumentation capable of the experiments described here; (6) emphasis may still have to be put on the more precise description of the incoherent background (cf. Fig. 1), so that the functional form could be applied for correcting data taken at neutron diffractometers without polarization analysis (as opposed to measuring more and more samples—there may not be enough beam time for practicing both kinds of activities freely). To this end, the incoherent intensities presented here can provide a rather encouraging initial step towards a reference set of spin-incoherent backgrounds measured for

materials with varying ^{1}H content, and for molecules of different chemical behavior.

[1] W. E. Thiessen and A. H. Narten, Neutron diffraction study of light and heavy water mixtures at 25 °C, J. Chem. Phys. **77**, 2656 (1982).

[2] A. K. Soper, F. Bruni, and M. A. Ricci, Site–site pair correlation functions of water from 25 to 400 °C: Revised analysis of new and old diffraction data, J. Chem. Phys. **106**, 247 (1997).

[3] G. Hura, D. Russo, R. M. Glaeser, T. Head-Gordon, M. Krack, and M. Parinello, Water structure as a function of temperature

from x-ray scattering experiments and *ab initio* molecular dynamics, Phys. Chem. Chem. Phys. **5**, 1981 (2003).

[4] A. Zeidler, P. S. Salmon, H. E. Fischer, J. C. Neuefeind, J. M. Simonson, H. Lemmel, H. Rauch, and T. E. Markland, Oxygen as a site specific probe of the structure of water and oxide materials, Phys. Rev. Lett. **107**, 145501 (2011).

[5] E. Schwegler, G. Galli, and F. Gygi, Water under pressure, Phys. Rev. Lett. **84**, 2429 (2000).

[6] P. Wernet, D. Nordlund, U. Bergmann, M. Cavallieri, M. Odelius, H. Ogasawara, L. Å. Häslund, T. K. Hirsch, L. Ojemäe, P. Glatzel, L. G. M. Pettersson, and A. Nilsson, The structure of the first coordination shell in liquid water, Science **304**, 995 (2004).

[7] T. Head-Gordon and M. E. Johnson, Tetrahedral structure or chains for liquid water, Proc. Natl. Acad. Sci. USA **103**, 7973 (2006).

[8] L. Pusztai, Partial pair correlation functions of liquid water, Phys. Rev. B **60**, 11851 (1999).

[9] V. F. Sears, Neutron scattering lengths and cross sections, Neutron News **3**, 26 (1992).

[10] J. G. Powles, J. C. Dore, and D. I. Page, Coherent neutron scattering by light water (H_2O) and a light-heavy water mixture (64 percent H_2O/36 percent D_2O), Mol. Phys. **24**, 1025 (1972).

[11] L. Blum and A. H. Narten, *Diffraction by Molecular Liquids*, edited by I. Prigogine and S. A. Rice, Advances in Chemical Physics Vol. 34 (John Wiley & Sons, Inc., New York, 1976), pp. 203–243.

[12] J. G. Powles, Slow neutron scattering by molecules, V. Recoil corrections for any molecule, Mol. Phys. **37**, 623 (1979).

[13] J. R. Granada, V. H. Gillette, and R. E. Mayer, Calculation of neutron cross sections and thermalization parameters for molecular gases using a synthetic scattering function. I, Phys. Rev. A **36**, 5585 (1987).

[14] J. Dawidowski, J. R. Granada, R. E. Mayer, G. J. Cuello, V. H. Gillette, and M.-C. Bellissent-Funel, Multiple scattering and inelasticity corrections in thermal neutron scattering experiments on molecular systems, Physica B **203**, 116 (1994).

[15] L. A. Rodríguez Palomino, J. Dawidowski, J. J. Blostein, and G. J. Cuello, Data processing method for neutron diffraction experiments, Nuclear Instrum. Methods Phys. Res., Sect. B **258**, 453 (2007).

[16] *Polarized Neutron Scattering*, edited by Th. Brückel and W. Schweika, *Schriften des Forschungszentrums Jülich, Reihe Materie und Material/Matter and Materials* Vol. 12, (Forschungszentrum Jülich GmbH, 2002).

[17] J. C. Dore, J. H. Clarke, and J. T. Wenzel, Separation of coherent and spin-incoherent neutron scattering by polarization analysis, Nucl. Instrum. Methods **138**, 317 (1976).

[18] L. Temleitner, L. Pusztai, and W. Schweika, The structure of liquid water by polarized neutron diffraction and reverse Monte Carlo modeling, J. Phys. Condens. Matter **19**, 335207 (2007).

[19] E. Lelièvre-Berna, E. Bourgeat-Lami, Y. Gilbert, N. Kernavanois, J. Locatelli, T. Mary, G. Pastorello, A. Petukhov, S. Pujol, R. Rouques, F. Thomas, M. Thomas, and F. Tasset, ILL polarised hot-neutron beam facility D3, Physica B **356**, 141 (2005).

[20] R. Surkau, J. Becker, M. Ebert, T. Grossmann, W. Heil, D. Hofmann, H. Humblot, M. Leduc, E. W. Otten, D. Rohe, K. Siemensmeyer, M. Steiner, F. Tasset, and N. Trautmann,

Realization of a broad band neutron spin filter with compressed, polarized ^3He gas, Nuclear Instrum. and Methods Phys. Res., Sect. A **384**, 444 (1997).

[21] W. Heil, K. H. Andersen, R. Cywinski, H. Humblot, C. Ritter, T. W. Roberts, and J. R. Stewart, Large solid-angle polarization analysis at thermal neutron wavelengths using a ^3He spin filter, Nuclear Instrum. and Methods Phys. Res., Sect. A **485**, 551 (2002).

[22] L. B. McCusker, R. B. Von Dreele, D. E. Cox, D. Louër, and P. Scardi, Rietveld refinement guidelines, J. Appl. Crystallogr. **32**, 36 (1999).

[23] J. Dawidowski and G. J. Cuello, Experimental corrections in neutron diffraction of ambient water using H/D isotopic substitution, J. Phys.: Conf. Series **340**, 012004 (2012).

[24] G. Placzek, The scattering of neutrons by systems of heavy nuclei, Phys. Rev. **86**, 377 (1952).

[25] M. A. Howe, R. L. McGreevy, and W. S. Howells, The analysis of liquid structure data from time-of-flight neutron diffractometry, J. Phys.: Condens. Matter **1**, 3433 (1989).

[26] A. C. Hannon, W. S. Howells, and A. K. Soper, A suite of programs for the analysis of time-of-flight diffraction data from liquid and amorphous samples, Inst. Phys. Conf. Series **107**, 193 (1990).

[27] A. K. Soper, Inelasticity corrections for time-of-flight and fixed wavelength neutron diffraction experiments, Mol. Phys. **107**, 1667 (2009).

[28] L. Pusztai and R. L. McGreevy, MCGR: An inverse method for deriving the pair correlation function from the structure factor, Physica B **234-236**, 357 (1997).

[29] O. Gereben, P. Jóvári, L. Temleitner, and L. Pusztai, A new version of the RMC++ reverse Monte Carlo programme, aimed at investigating the structure of covalent glasses, J. Optoelectron. Adv. Mater. **9**, 3021 (2007).

[30] R. L. McGreevy and L. Pusztai, Reverse Monte Carlo simulation: A new technique for the determination of disordered structures, Mol. Simul. **1**, 359 (1988).

[31] A. K. Soper, Disordered atom molecular potential for water parameterized against neutron diffraction data. Application to the structure of ice Ih, J. Phys. Chem. B (2015).

[32] J. Teixeira, in *Correlations and Connectivity*, edited by H. E. Stanley and N. Ostrowsky, NATO ASI Series Vol. 188 (Kluwer Academic Publishers, Dordrecht, 1990), pp. 167–187.

[33] A. K. Soper and C. J. Benmore, Quantum differences between heavy and light water, Phys. Rev. Lett. **101**, 065502 (2008).

[34] W. B. O'Dell, D. C. Baker, and S. E. McLain, Structural evidence for inter-residue hydrogen bonding observed for cellobiose in aqueous solution, PLoS ONE **7**, e45311 (2012).

[35] E. Scoppola, A. Sodo, S. E. McLain, M. A. Ricci, and F. Bruni, Water-peptide site-specific interactions: A structural study on the hydration of glutathione, Biophys. J. **106**, 1701 (2014).