The microscopic structure of the hydrogen liquids

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Abstract
We have measured the microscopic structure of liquid para-hydrogen by means
of a neutron diffraction experiment on the D4C liquids diffractometer at
Institute Laue-Langevin (Grenoble, France). This is the first direct neutron
diffraction measurement of the static structure factor of hydrogen. The present
determination of the microscopic structure of hydrogen is consistent with
previous experimental determinations carried out on liquid deuterium and with
path integral Monte Carlo simulations. The comparison with recent x-ray
determinations is also satisfactory.

1. Introduction

It is common to attribute the emergence of quantum effects to the space delocalization of
the particles. In fact, for quantum particles, the centre-of-mass position cannot be associated
any longer with individual points in space, as in the classical case, but is characterized by a
probability distribution [1, 2]. For free particles, the probability distribution is Gaussian and
its width is given by the de Broglie thermal wavelength, λ_{DB}, which is defined as [3]:

$$\lambda_{DB} = h/(2\pi M k_B T)^{1/2} \tag{1}$$

where M is the particle mass, T is the temperature, and k_B is the Boltzmann constant. For
the hydrogen liquids, λ_{DB} is comparable with the hard-core size of the molecule, thus giving
rise to rather large quantum delocalization effects (see, for example, table 1 of [4]). However,
its ratio to the average intermolecular distance remains small with respect to that observed for
helium at the λ-transition, which implies negligible exchange effects. Thus, the hydrogens can
be considered, to all practical purposes, as genuine Boltzmann quantum liquids.

Table 1. Comparison between the relevant thermodynamic parameters of the hydrogen isotopes; CP = critical point, TP = triple point [6, 7].

Isotope	T_{TP} (K)	p_{TP} (bar)	n_{TP} (nm^{-3})	T_{CP} (K)	p_{CP} (bar)	n_{CP} (nm^{-3})
H_2	13.803	0.07	23.01	32.976	12.93	9.39
D_2	18.71	0.17	26.00	38.34	16.65	10.44

It is generally assumed that the electronic structures of the molecular hydrogen isotopes are very similar, even though minor variations are expected as evidenced, for example, by the slightly different values of the molecular quadrupole (and higher-order multipole) moments. At any rate, the deviations are very small and the intermolecular potentials of the hydrogen isotopes are generally considered to be almost equal [5]. Assuming that hydrogen and deuterium experience the same intermolecular potential, the only difference between the two systems resides in the different molecular mass. This implies a relatively large change in the value of λ_{DB} and, consequently, large differences are expected in the thermodynamic and structural properties of their condensed phases. It is a fact that the critical temperatures of the two isotopes differ by some 16%, while the difference becomes almost 36% for the triple-point temperature (see table 1). The corresponding variations, at the level of the microscopic structural features, were for a long time unknown. In view of this, we embarked, several years ago, on a series of measurements of the microscopic structure factors of the two hydrogen isotopes. We are now in the position to present a first account of this comparison.

2. Historical survey

A neutron diffraction measurement of the microscopic structure factor of the hydrogen liquids is not an easy task. Apart from the presence of the intramolecular degrees of freedom and the inelasticity effects associated with them, the recoil effects, whose size is determined by the ratio between the neutron and the nuclear mass [8], are so large that the usual correction techniques become useless for the case of the hydrogens. However, the recent development of the modern pulsed neutron sources and the use of time-of-flight neutron diffraction has allowed the problem to be faced with some success. The first reliable neutron diffraction measurements of the microscopic structure of liquid deuterium is relatively recent and was carried out using the small-angle, time-of-flight, liquids diffractometer SANDALS at ISIS (UK). The structure factor of liquid deuterium was measured in the vicinity of the triple point [9] and close to the freezing transition [10]. An important consequence of these experiments was the extension of the Young and Koppel model [11] to the condensed phases of the hydrogens [12]. This has allowed a better evaluation of the inelastic scattering corrections and a subsequent neutron diffraction experiment carried out on 7C2, the liquids diffractometer of the Laboratoire Leon Brillouin (Saclay, France) [13], led to a significant improvement in the experimental data.

The knowledge of the microscopic structure factor of deuterium, however, is not easily extended to hydrogen. Also from the experimental point of view, it is not easy to extend to hydrogen the experience gained with the heavier isotope. In addition to the larger size of the recoil effects, due to the halved molecular mass, one has to face also the overwhelming size of the incoherent proton cross-section. This makes it extremely difficult, in a neutron diffraction experiment, to extract the intermolecular response, which carries the structural information, from the large intramolecular contribution. A first experimental attempt to obtain information on the microscopic structure of liquid hydrogen, still on SANDALS, aimed to determine the thermodynamic derivatives of $S(Q)$ [4]. However, it was again a standard reactor source
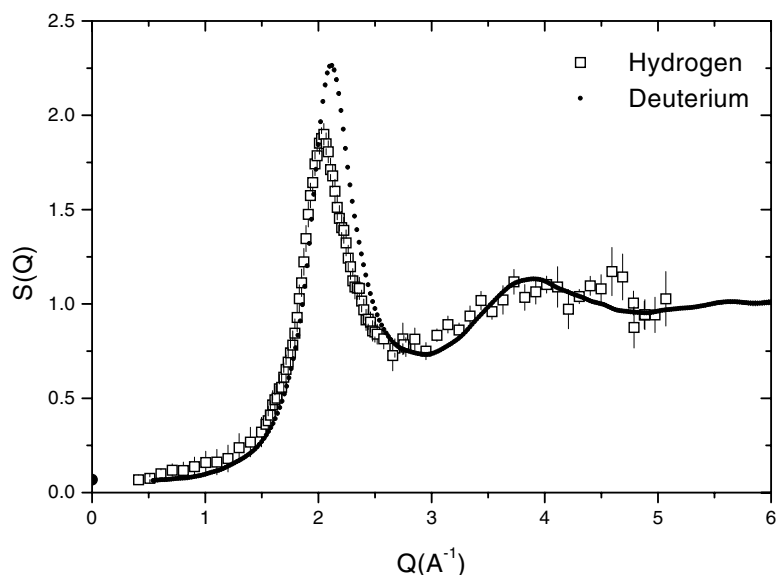
Figure 1. Microscopic structure factors of hydrogen liquids close to the triple point. The open squares represent the hydrogen data ($T = 17.1$ K, $n = 22.95$ nm^{-3}) [14], while the black dots relate to deuterium ($T = 20.7$ K and $n = 25.42$ nm^{-3}) [13]. The full dot at $Q = 0$ is obtained from the thermodynamic compressibility.

experiment carried out on D4C, the liquids diffractometer of the Institute Laue-Langevin (Grenoble, France), that gave a quantitative answer to the problem of the structure factor [14].

3. The structure factor of the hydrogen liquids

The above-mentioned experiments have permitted a quantitative determination of the microscopic structure factor of the hydrogen liquids in similar thermodynamic conditions (i.e. rather close to their respective triple points). The results are reported in figure 1. For hydrogen, the temperature is $T = 17.1$ K with a density $n = 22.95$ nm^{-3} ($n/n_{TP} = 0.998$). For deuterium, $T = 20.7$ K and $n = 25.42$ nm^{-3} ($n/n_{TP} = 0.978$).

Even though affected by larger errors, the hydrogen data appear slightly shifted to lower Q-values. This is consistent with a larger size of the quantum effects which produces, in r-space, a broader single-particle distribution function [15] with a consequent increase of the effective diameter of the hydrogen molecule with respect to deuterium. As a consequence, this would produce a somewhat expanded radial distribution function which, in Q-space, is reflected by a shift to lower Q-values of the rising edge of the structure factor. Another feature which is apparent from figure 1 is the amplitude of the main peak of liquid hydrogen which appears substantially lower than that of deuterium. This is most probably produced by the lower density of hydrogen close to the triple point. However, a lower main peak in the structure factor is also expected as a consequence of a more extensive zero-point motion of the hydrogen molecules which implies broader peaks in the radial distribution function [16].

The measured structure factor of deuterium turns out to be in excellent agreement with path integral Monte Carlo (PIMC) simulation results [17]. For hydrogen, the agreement is less spectacular but still rather good on a quantitative basis [14]. This is a remarkable result, taking into account the well-recognized experimental difficulties.
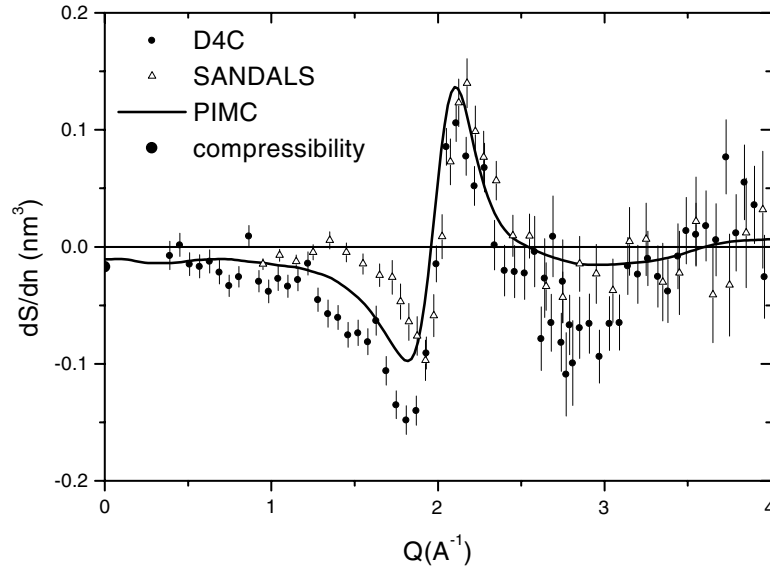
Figure 2. The density derivative, at constant temperature, of the structure factor of liquid hydrogen. The full circles represent the D4C experimental results [14], while the open triangles relate to the SANDALS experiment reported in [4]. The PIMC results (full curve) are taken from [27]. The full dot at $Q = 0$ is obtained from the thermodynamic compressibility.

It is interesting to compare the present experimental results with other determinations available in the literature. For deuterium, the only other neutron diffraction results were due to old experiments [18] of doubtful reliability [19]. For hydrogen, there were no neutron diffraction results prior to our experiment. However, alternative methods of determining the structure factor of liquid hydrogen using neutron scattering were attempted. Bermejo and co-workers [20] have reported a result for the structure factor of liquid para-hydrogen obtained using data from an inelastic neutron scattering experiment and the sum rule which relates the dynamic structure factor, $S(Q, \omega)$, to the static one, $S(Q)$ [21]:

$$S(Q) = \int_{-\infty}^{+\infty} d\omega \, S(Q, \omega). \tag{2}$$

Their results are qualitatively reasonable, but show an anomalously intense main peak of $S(Q)$, which exceeds the value of 2.85 that was defined by Hansen and Verlet [22] as corresponding to the onset of the freezing transition for a Lennard-Jones liquid. We have no reason to believe that the measured dynamic structure factor of hydrogen [23] is incorrect, also because the inelastic spectra are in fair quantitative agreement with a recent quantum mode coupling theoretical calculation by Reichman and Rabani [24]. However, it is a fact that the static structure factor derived by Bermejo *et al* [20] is different from our present results and is also at variance with the PIMC simulation data [16].

More recently, x-ray experiments [25, 26] performed at ESRF, the European Synchrotron Radiation Facility (Grenoble, France), used the same method, i.e. integrating the dynamic structure factor at constant Q, to determine the microscopic structure factor. These experiments were carried out on liquid hydrogen at $T = 31.5$ K and a density of $n = 21.5$ nm^{-3} by Pratesi *et al* [25], and at $T = 20$ K and a density of $n = 21.24$ nm^{-3} by Cunsolo *et al* [26]. In both cases, an x-ray diffraction measurement, carried out in parallel, showed substantially similar results with much lower error bars. Moreover, in both cases, the x-ray experimental data give

a main peak of $S(Q)$ markedly lower than 2 and consistent with the PIMC simulation results. The same technique was also used to measure $S(Q)$ of liquid deuterium [26] which, again, turned out to be in good agreement with the PIMC simulations.

4. The density derivative of the structure factor

The present hydrogen experiment was carried out at several thermodynamic points, thus allowing us to determine the density derivative of the structure factor. This quantity was also measured in a previous independent experiment [4] and the two results are compared in figure 2, together with the results of the PIMC simulations taken from [27]. The data appear rather noisy and not fully consistent in the low Q-region, even though the overall agreement among the three sets of data is satisfactory. In particular, in the Q-region below the main peak position the observed differences are larger than the reported experimental errors, which indicates that, in both experiments, some residual systematic errors are probably still present. However, it is reassuring to note that the simulation results seem to fall in between the two experiments.

Another interesting feature, common to both the experimental data sets, is the slight shift, toward higher Q-values, of the rising edge of the density derivative. This effect would suggest that the true space-scaling parameter (a sort of effective molecular diameter) is smaller than that predicted by the simulation. Apparently, this result seems to be peculiar to hydrogen and is not confirmed by the corresponding quantity for deuterium, where an almost perfect agreement was found [17]. This could be attributed to the larger quantum effects of hydrogen with respect to those of deuterium. However, the large observed uncertainties of the experimental data suggest maintaining a conservative view, even though the two independent experiments seem to give a coherent picture of this particular effect.

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