

Microscopic structure factor of liquid para-hydrogen

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(Received 14 November 2001; published 13 February 2002)

We have calculated, by means of path integral Monte Carlo (PIMC) simulations, the microscopic structure factor of liquid para-hydrogen at $T=15.7$ K. The present simulation results are compared with a recent experimental determination of the structure factor at a similar thermodynamic state, as well as with a previous path integral centroid molecular dynamics (PICMD) simulation. The comparison is less than satisfactory. While the PICMD results are not consistent with the PIMC data, also the experimental results do not quantitatively agree with the present simulations and are not of the accuracy level attainable for other simple liquids.

DOI: 10.1103/PhysRevB.65.092204

PACS number(s): 67.20.+k, 61.12.-q, 61.20.Ja

In spite of the simple molecular structure of hydrogen and its importance, both from the fundamental and the applicative point of view, the microscopic structural properties of the liquid phase have not yet been experimentally measured to the desired level of accuracy. In fact, while detailed microscopic structural data are available for the heavier isotope, liquid deuterium,¹ this structural information is not easily transferred to the lighter isotope, due to the different role played by quantum effects.² In particular, no reliable experimental information was available on the microscopic structure factor of the hydrogen liquids until 1993.³

Due to the small number of electrons, an x-ray determination of the structure factor of the hydrogens is not an easy task. A neutron diffraction experiment, on the other hand, is equally difficult. The influence of recoil effects, whose size is determined by the ratio between the neutron and the molecular mass,⁴ affects the experimental neutron cross section of the hydrogens to such a degree that it is difficult to extract the relevant information. For these reasons, the first reliable neutron diffraction measurement of the microscopic structure of dense deuterium gas is relatively recent and was carried out using only the small-angle scattering detectors of a standard powder diffractometer at the pulsed neutron source ISIS (UK).⁵ Later, taking advantage of the availability of a new small-angle neutron diffractometer for amorphous and liquid systems (SANDALS, at ISIS), the structure factor of liquid deuterium could be measured in the vicinity of the triple point³ and close to the freezing transition.⁶ Once the know-how was established, a neutron diffraction experiment on liquid deuterium was also carried out on a standard reactor source,⁷ which allowed an improvement of the quality of the experimental results. In fact, the inelasticity corrections for the two experiments are located in different spectral regions and, therefore, from a critical comparison of the two experiments, it was possible to perform an accurate determination of the structure factor of liquid deuterium which, in turn, was in excellent agreement with path integral Monte Carlo (PIMC) simulation results.¹

Thus, while the experimental structure factor of liquid deuterium is known with good accuracy, analogous information for hydrogen is still missing due to basic experimental difficulties, especially when using neutron scattering. In fact, apart from the smaller molecular mass, which leads to larger

inelasticity corrections, it is the unfavorable ratio between the coherent and incoherent cross sections of hydrogen which makes the experimental determination of the microscopic structure of light hydrogen so difficult. As a consequence, the coherent scattering contribution, which contains the relevant information on the intermolecular structure, is almost invisible under an overwhelming incoherent background.

It was therefore most gratifying to observe that in a recent paper⁸ Bermejo and co-workers were able to obtain this information with an acceptable level of accuracy. In fact, Bermejo *et al.* did not measure the structure factor of hydrogen directly by means of a neutron diffraction experiment. Instead, they measured the dynamic structure factor $S(k, \omega)$ and utilized the sum rule which relates it to the static structure factor $S(k)$,⁹

$$S(k) = \int_{-\infty}^{+\infty} d\omega S(k, \omega). \quad (1)$$

Thus, from an experimental measurement of the double-differential neutron cross section of hydrogen, which is related to $S(k, \omega)$,¹⁰ it is possible to derive the microscopic structure factor. Bermejo *et al.*⁸ also compared the experimental data for $S(k)$ with simulation results obtained from both a path integral centroid molecular dynamics (PICMD) and a classical molecular dynamics (MD) simulation. The comparison was reasonable, considering that the PICMD simulation gives a much better position for the main peak of $S(k)$ than the classical system (cf. Fig. 1 of Ref. 8). However, the results reported by Bermejo *et al.* are not satisfactory from several points of view. First, the experimental values of $S(k)$ appear too high in the region of the first peak. In the early days of computer simulation, one of the accepted indicators for the liquid-solid phase transition was the so-called Hansen-Verlet criterion;¹¹ it states that, when the first peak of $S(k)$ exceeds the value of 2.85, then the liquid sample is on the onset of the freezing transition. Even if the Hansen-Verlet criterion was formulated for simple model systems (classical monatomic particles interacting through a Lennard-Jones potential) it is hard to believe that $S(k)$ of hydrogen, a genuine quantum system for which one expects a general broadening and damping of the structural features,

should reach such a large value in the liquid phase. This fact is related to the second problem: Due to the expected structural broadening, the height of the peak of $S(k)$ in the quantum simulation results should be *lower* than its classical counterpart, whereas just the opposite is the case in Fig. 1 of Ref. 8. In fact, by comparing the results presented by Bermejo *et al.* with a similar picture given by Kinugawa (Fig. 1 of Ref. 12), it appears clearly that PICMD does give a lower value for the main peak of the quantum $S(k)$ with respect to the classical case. Last, but not least, in spite of the small difference in the thermodynamic conditions, in the quantum calculation reported by Kinugawa,¹² the peak height of $S(k)$ is *below* the value of 2, while in the paper by Bermejo *et al.*, this peak height is well above the level of 2. Furthermore, for the classical calculation, Kinugawa's $S(k)$ peaks at ≈ 3 , which is acceptable since *classical* hydrogen would be solid under those thermodynamic conditions, while *real* hydrogen remains liquid due to the large effect of the zero-point motion.

In summary, the recent results by Bermejo *et al.*,⁸ rather than solving a long-standing problem, seem to raise serious questions about the experimental and, in particular, the simulation data. Their results are also at variance with our previous findings, where we were able to achieve an almost perfect agreement between our neutron diffraction data for liquid deuterium and the PIMC simulations.¹ For these reasons, we decided to perform independent PIMC simulations on liquid hydrogen to shed light, if possible, on the origin of these discrepancies, as the experimental aspect is more difficult to resolve. An additional motivation for performing the present calculations is given by the very good agreement of previous quantum mechanical simulations with the thermodynamic derivatives of $S(k)$ for both the hydrogen isotopes: i.e., deuterium *and* hydrogen. These, too, were determined by neutron scattering experiments and compared well with the corresponding PIMC results.^{13,14}

The present simulations were carried out using both the isotropic component of the phenomenological pair potential derived by Norman *et al.*¹⁵ (NWB) and the Silvera-Goldman (SG) potential.¹⁶ Both potentials are reliable, with the NWB which is more oriented to the pair interactions and the SG potential which takes into account, in an effective way, many-body interactions. The first one was previously used by us obtaining excellent agreement with the experimental structure factor of liquid deuterium.¹ In addition, we had already used the NWB potential in simulations of hydrogen, and we obtained reasonable agreement for the thermodynamic derivatives of $S(k)$ of liquid para-hydrogen.¹⁴ However, since Bermejo *et al.*⁸ used SG, we decided to perform our simulations using the same model, in order to avoid any possible effect attributable to a different choice of the potential. At any rate, we found that the simulation results are almost independent from the particular choice of the pair interaction. In the following, for the sake of simplicity, we will report only the results obtained with the SG potential.

The PIMC simulations were implemented using the primitive algorithm¹⁷ and Trotter numbers $P=2,4,8,16$, and 32. The convergence to the quantum mechanical limit was verified by monitoring the behavior of the pair correlation

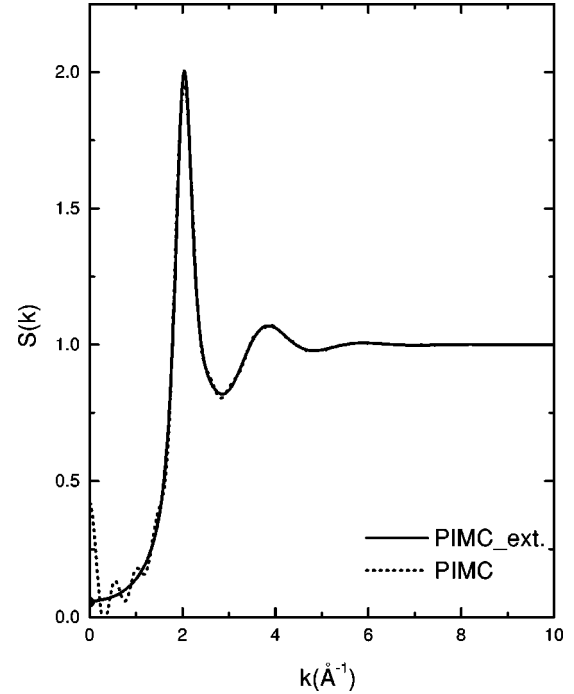


FIG. 1. Microscopic structure factor of liquid para-hydrogen at $T=15.7$ K and $n=22.8$ nm⁻³. The dashed line is obtained by direct transformation of the radial distribution function obtained from the simulation. The solid line is obtained by extending the simulation $g(r)$ by Verlet's recipe (see text). The solid circle at $k=0$ is derived from the experimental compressibility of liquid hydrogen.

function, $g(r)$, as a function of P . We found that for liquid hydrogen at $T=15.7$ K (number density $n=22.8$ nm⁻³) it was necessary to extend the Trotter number up to a maximum of $P=32$, while, for the case of liquid deuterium, $P=16$ was sufficient.¹

The basic simulation output, i.e., the radial distribution function for the molecular centers of mass, was limited to intermolecular distances less than some maximum value R_{\max} . This upper limit is determined by half the edge length of the simulation box which, in our case, using $N=560$ particles and the density stated above, turns out to be ≈ 13.6 Å. However, in order to calculate the structure factor, $g(r)$ has to be extrapolated to higher r values since, for an isotropic liquid, $S(k)$ is related to the radial distribution function by the expression

$$S(k) = 1 + \frac{4\pi n}{k} \int_0^{\infty} dr r \sin(kr) h(r), \quad (2)$$

where $h(r) = g(r) - 1$. The factor r in the integral amplifies the asymptotic behavior of $h(r)$ and, if this function is not smoothly extrapolated for $r > R_{\max}$, the truncation may produce spurious oscillations in $S(k)$, especially in the low- k region. In fact, this problem severely affects the quantum simulation data reported in Fig. 1 of Ref. 8.

A simple and well-established procedure of extrapolating $g(r)$ beyond R_{\max} is the recipe by Verlet,¹⁸ who suggests to

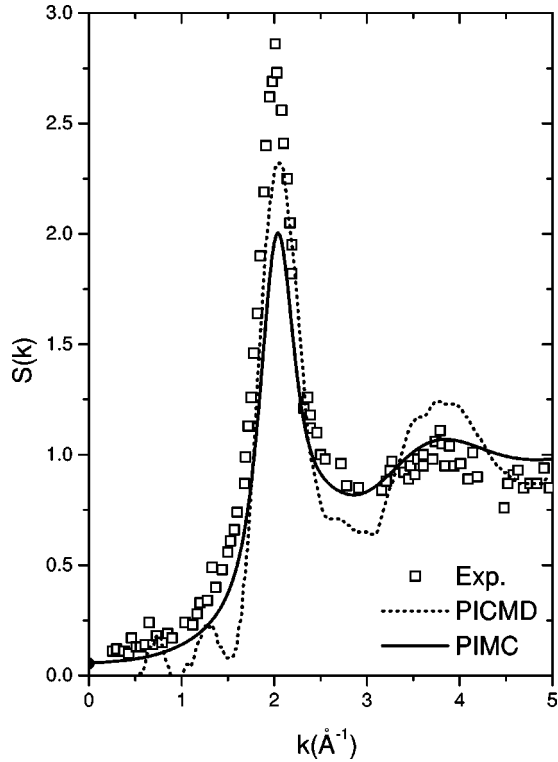


FIG. 2. Comparison between the present PIMC simulation results (solid line) and the data of Ref. 8; the experimental data are represented by the open squares, while the dotted line represents the PICMD simulation data. The solid circle at $k=0$ represents the experimental compressibility limit derived from the thermodynamic data.

approximate the asymptotic behavior of $h(r)$ using a damped oscillatory function of the form

$$h(r) \sim (A/r) \exp(-r/r_0) \sin(r/r_1). \quad (3)$$

The parameters A , r_0 , and r_1 were obtained by fitting the functional form (3) to the simulation results, starting from the third zero of $h(r)$, i.e., at $r \approx 6$ Å. In this way, we could extrapolate the simulation results for $g(r)$ and eliminate the spurious oscillations from $S(k)$. The structure factor so obtained is shown in Fig. 1 (solid line). The dashed line shows the calculated $S(k)$ using the raw simulation output. It is well known that truncation errors can significantly affect the calculated structure factor, especially in the low- k region up to, and including, the height of the main peak. In particular, the value at $k=0$, $S(0)=0.42$, is almost one order of magnitude larger than the experimental value derived from the compressibility and represented by the solid circle in the figure. The Verlet extrapolation, on the other hand, drastically reduces the truncation errors and brings the calculated $S(0)$ very close to the thermodynamic limit.¹⁹ In this case, the simulation result $S(0)=0.061$ agrees well with the experimental value of 0.054.

In Fig. 2 we compare the present simulation results for $S(k)$ with the data reported by Bermejo and co-workers.⁸ As far as the experimental data are concerned, the agreement cannot be claimed to be more than qualitative. In practice,

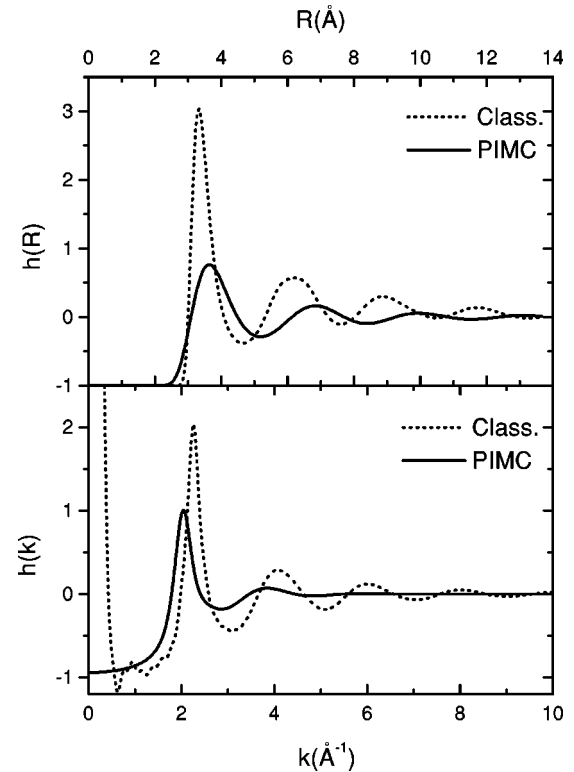


FIG. 3. Effect of quantum corrections on the pair distribution function of liquid hydrogen. The figure shows the raw simulation data $h(r)=g(r)-1$ and their spatial Fourier transform $h(k)=S(k)-1$ for the classical simulation and the quantum mechanical limit. The broadening of the radial distribution corresponds, in k space, to a decrease of the main peak. The shift towards larger distances of the peaks in $h(r)$ corresponds to a decrease of the periodicity in k space and to a consequent shift of the main peak of $h(k)$ to lower k values.

the two sets of data agree only in the position of the peaks of $S(k)$, while the amplitudes of the oscillations are quantitatively different, with the experimental points significantly exceeding the simulation results in the region of the main peak. As noted above, the present simulation data converge smoothly to the experimental¹⁹ compressibility value, while the experimental data appear rather large in the entire low- k region. Basing on our previous experience with liquid deuterium, the observed differences seem too large to be real.

From Fig. 2 we note that also the PICMD simulation data do not agree with the present PIMC results. As already noted by the authors, the quantum mechanical $S(k)$ of Bermejo *et al.* is severely distorted by truncation errors. However, even allowing for these effects, the remaining discrepancies seem too large. Also, even though this is irrelevant for the discussion of the experimental situation, the classical simulation results shown for comparison in Fig. 1 of Ref. 8 definitely must be wrong. It is well known (and intuitively obvious) that the peaks of $g(r)$ increase in width and decrease in height as one goes from the classical to the quantum mechanical fluid. As a consequence, peak amplitudes in the quantum mechanical $S(k)$ should be lower than those in the classical case. The simulation data reported by Bermejo *et al.*, instead, show the opposite trend. In order to demon-

strate this point explicitly, we compare in Fig. 3 the classical simulation with the quantum PIMC results. The upper part of the figure contrasts the classical $h(r)$ with its quantum mechanical counterpart. As expected, the quantum function shows broader and lower peaks which are shifted to larger distances due to delocalization of the particles. This behavior is reflected in k space by broader and lower peaks which are shifted towards smaller k values (cf. the lower part of the figure). We observe that the number of pronounced oscillations of $S(k)$ decreases significantly while the position of the main peak moves from $k=2.26 \text{ \AA}^{-1}$, for the classical case, to $k=2.04 \text{ \AA}^{-1}$ in the quantum structure factor.

In summary, we have reported PIMC simulations of the microscopic structure factor of liquid para-hydrogen using the Silvera-Goldman intermolecular pair potential. The present simulation results do not agree with the data published by Bermejo *et al.*,⁸ both at the level of the experimental results and the simulations reported in Ref. 8. In our opinion, based also on our experience with the structure factor of liquid deuterium, the differences observed for hydrogen are too large to be real. We have previously used the same PIMC

simulation program (except for the different mass of the isotopes) to successfully predict the structure factor of liquid deuterium, using the NWB intermolecular potential. It is difficult to imagine that the simulations which were so successful for deuterium should give qualitatively incorrect results for liquid hydrogen, when the greater importance of quantum effects in hydrogen is accounted for by using a greater Trotter number. We have also checked that the use of a different intermolecular model potential (i.e., SG versus NWB) does not change the results in a significant way. The only other approximation we have made is the assumption of Boltzmann statistics, but exchange effects are negligible, certainly for deuterium and most likely for hydrogen, at these relatively high temperatures.

Thus, while the simulation results of Bermejo *et al.*⁸ are, at least, partially incorrect, we feel that also the experimental data are not sufficiently reliable to serve as a reference for theoretical calculations. However, we want to stress again that the experimental measurement of the microscopic structure of liquid hydrogen is a difficult task and further experimental efforts are needed to solve the problem to a satisfactory level of accuracy.

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