

Microscopic Structure and Intermolecular Potential in Liquid Deuterium

M. Zoppi and U. Bafile

Istituto di Elettronica Quantistica, Consiglio Nazionale delle Ricerche via Panciatichi 56/30, I-50127 Firenze, Italy

E. Guarini and F. Barocchi

Dipartimento di Fisica, Università degli Studi di Firenze, Largo E. Fermi, 2 I-50125 Firenze, Italy

R. Magli

Dipartimento di Energetica, Università degli Studi di Firenze, via di S. Marta, I-50139 Firenze, Italy

M. Neumann

Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

(Received 28 March 1995)

We have measured the intermolecular structure factor and its thermodynamic derivatives in the vicinity of the triple point of liquid deuterium, using two different neutron sources. We have also derived the same quantities by using path integral Monte Carlo computer simulations. For the structure factor, we find good agreement between the experiments and the simulation results, using either the Lennard-Jones or a more realistic phenomenological potential. However, when the comparison is extended to the thermodynamic derivatives, a clear difference is observed between the two different intermolecular potentials.

PACS numbers: 61.25.Em, 61.12.Gz, 61.20.Gy

The qualitative behavior of the structure factor $S(Q)$ in simple liquids is dominated by excluded volume effects. Nevertheless, it has been shown recently [1] that a precise neutron scattering determination of $S(Q)$ provides information on the basic molecular interactions allowing, in particular, a test on the pair interaction model and some estimate of the irreducible three-body potential term. In addition, it has been shown that the density derivative of $S(Q)$ is much more sensitive to the details of the interaction model than the function itself. For example, a difference of more than 50% was obtained between two different model potentials of krypton, in the liquid phase near the triple point [1]. Detailed knowledge of the microscopic structure of liquids is also a necessary input of the present freezing theories for both classical and quantum systems [2–6].

The importance of experimentally determining structural quantities in quantum fluids is enhanced by the consideration that, at the present time, the development of computer simulation methods allows one to deal theoretically with a quantum system by using the path integral Monte Carlo (PIMC) technique [7]. It is important to notice that, despite the several neutron diffraction experiments on liquid helium [8–10], no high precision comparison with simulations has been carried out on quantum liquids.

Motivated by the previous considerations, we have performed a set of neutron diffraction measurements on liquid deuterium in the vicinity of the triple point. Two different instruments have been used, namely, the time-of-flight (TOF) diffractometer SANDALS at the pulsed neutron source ISIS (U.K.) [11] and the two-

axis diffractometer 7C2 at the thermal neutron source of Laboratoire Léon Brillouin [12] (France).

It is well known that different regions of Q are affected by inelastic scattering for the two diffraction techniques. Moreover, the calculation of inelastic corrections for liquid deuterium can be carried out accurately for a monochromatic thermal neutron source, while it is almost impossible for a pulsed source [11]. For these reasons, it was decided to collect diffraction data on both diffractometers. The two independent determinations of the center-of-mass structure factor, relative to the same thermodynamic points, agree with each other within the statistical errors. Here we report the second set of data (7C2) which has better precision and is extended to lower Q values [13].

The experiment was done for seven thermodynamic states, four on the $T = 20.7$ K isotherm and four on the $n = 25.4 \text{ nm}^{-3}$ isochore, so that the thermodynamic derivatives of $S(Q)$ could be derived. The data were carefully corrected for absorption, multiple scattering, and inelastic scattering. The high- Q intramolecular contribution to the cross section was used for calibration purposes [14]. As will be seen in the following (cf. Figs. 1–3), the present experimental neutron data show a remarkable convergence toward the thermodynamic limits at $Q = 0$.

The experiments were then followed by a set of PIMC simulations performed at three of the seven thermodynamic points of the measurements. In this way, a meaningful comparison with the experiments could be accomplished, not only at the level of the microscopic structure factor, but also for its thermodynamic derivatives.

The simulations were carried out using two different choices for the pair interaction potential, namely, the simple Lennard-Jones (LJ) model ($\epsilon/k_B = 36.7$ K, $\sigma = 0.2959$ nm) and the isotropic component of the phenomenological potential derived by Norman, Watts, and Buck (NWB) for hydrogen [15]. This potential model is based on *ab initio* calculations, as well as on a number of solid state and molecular beam collision data, and should give a realistic description of the potential energy also for deuterium.

The PIMC algorithm was accomplished by extending the number of beads of the ring polymer, which in the classical isomorphism is equivalent to the quantum particle, up to a Trotter number $P = 16$ [16]. However, no real difference was observed between the $P = 8$ and $P = 16$ results. The simulation output, i.e., the radial distribution function for the molecular centers of mass, which extends up to half the size of the cubic box, was limited to a radius $r_c \approx 1.3$ nm. In order to compute a reliable structure factor, we had to extend the simulation results to higher values of r . In fact, for an isotropic liquid, the microscopic structure factor is related to the radial distribution function $g(r)$ by the space Fourier transform

$$S(Q) = 1 + (4\pi n/Q) \int_0^\infty dr r [g(r) - 1] \sin(Qr). \quad (1)$$

The r factor in the integral amplifies the tails of the $g(r)$, and therefore a suitable extension must be provided in order to evaluate $S(Q)$. The alternative (trivial) solution of increasing the number N of classical particles in the simulation is easily seen to be impractical since, in order to extend the cutoff radius from 1.3 to 3.0 nm, one must increase N from 500 to above 6000, which increases the simulation CPU time by more than 2 orders of magnitude.

According to the recipe given by Verlet [17], we have thus extended the function $h(r) = g(r) - 1$ by using a damped oscillating form

$$h(r) = (A/r) \exp(-r/r_0) \sin(r/r_1). \quad (2)$$

The parameters A , r_0 , and r_1 were obtained by fitting the functional form (2) to the simulation results, starting from the third zero of $h(r)$ [17].

Figure 1 shows the simulation results for $S(Q)$ and the comparison with the experiment, relative to the point at $T = 20.7$ K and $n = 25.4$ nm $^{-3}$ (for deuterium, the triple point is at $T = 18.71$ K and $n = 25.99$ nm $^{-3}$) [18]. We observe rather good agreement between the measured data and the results of both simulations, namely, the one carried out with the LJ model and that using the NWB potential, the latter showing overall slightly better agreement with the experiment.

When the comparison is extended to the thermodynamic derivatives of $S(Q)$ the difference between the two interaction models becomes evident. In Fig. 2, we re-

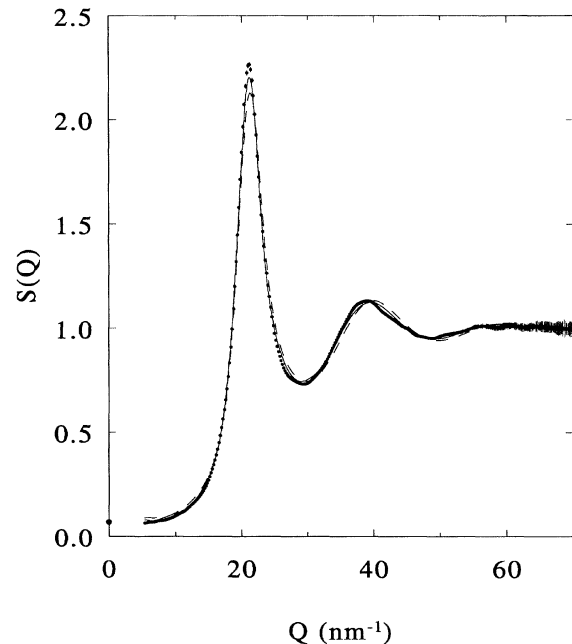


FIG. 1. Intermolecular structure factor $S(Q)$ of liquid deuterium at $T = 20.7$ K and $n = 25.4$ nm $^{-3}$. The dots refer to the present experimental data, and their error bars are visible when larger than the size of the points. The lines are the path integral Monte Carlo simulation results using the two different interaction potentials. The full line refers to the NWB phenomenological potential, while the dashed line is relative to the LJ model. The dot at $Q = 0$ is obtained from the compressibility value.

port the density derivative of $S(Q)$ on the $T = 20.7$ K isotherm evaluated at $n = 25.8$ nm $^{-3}$. The function is characterized by a large oscillation, in the region of the principal peak of $S(Q)$ around 20 nm $^{-1}$, and by smaller undulations at larger Q which are observed in both the experimental and simulation results. On the contrary, the oscillations in the simulations at low Q are attributed to an imperfect extrapolation of $g(r)$ to high r . The experiment gives a value for the full oscillation, between the minimum and the maximum of the function, of 0.25 nm 3 . The NWB simulation results give a quite similar value of 0.27 nm 3 , while the LJ result is 0.20 nm 3 . The difference between the two models, in this particular aspect, amounts to 35%, and a better agreement is observed for the NWB potential than for the LJ.

It is interesting to note that in the case of liquid Kr [1] an analogous conclusion was drawn about the superiority of the phenomenological potential by Aziz and Slaman [19], with respect to the LJ. However, in that case the amplitude of the main oscillation of the density derivative was larger for the LJ, while the opposite result is obtained for deuterium. Whether this is related to a much lower absolute temperature, or to a different influence of quantum effects, is unknown at present.

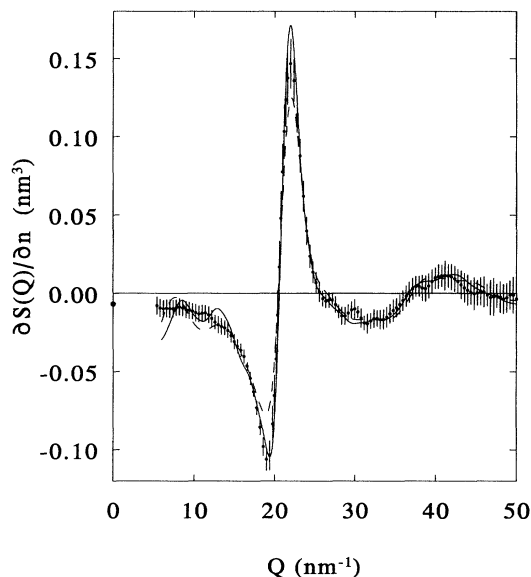


FIG. 2. Density derivative of the structure factor on the $T = 20.7$ K isotherm evaluated at $n = 25.8 \text{ nm}^{-3}$. The dots with the error bars are the present experimental results. The lines refer to the path integral Monte Carlo simulations. Their meaning is as in Fig. 1. We presume that the oscillations below 15 nm^{-1} are not real and are due to the not perfect extrapolation of the simulation results at large r . The dot at $Q = 0$ is obtained from the thermodynamic equation of state.

For the temperature derivative, evaluated at $T = 22.0$ K on the 25.4 nm^{-3} isochore and shown in Fig. 3, the difference between the two interaction models is much larger than the experimental uncertainties, and a clear distinction between the two models can be inferred. It is worthwhile to note that the results for the NWB potential are within the experimental error bars down to 15 nm^{-1} , where the spurious oscillations start to appear on both simulation models. Again, there is a strong difference between the two simulation results, with the LJ model resulting in a value for the amplitude of the main oscillations ($15 < Q < 30 \text{ nm}^{-1}$) that is roughly *one-half* of the value for the NWB potential.

Thus the superior reliability of the phenomenological NWB potential, with respect to the simple LJ model, emerges clearly from the comparison with the experimental information on thermodynamic derivatives of $S(Q)$, which appear to be much more sensitive than $S(Q)$ itself to the detailed form of the intermolecular potential.

In conclusion, we have shown that high accuracy determinations of the intermolecular structure factor in the liquid phase, when combined with its thermodynamic derivatives, provide information on the detailed shape of the pair interaction function even in a dense quantum fluid. The scattering function $S(Q)$ and its Fourier transform $g(r)$ are little sensitive to the details of the pair interaction potential. However, the thermodynamic derivatives allow

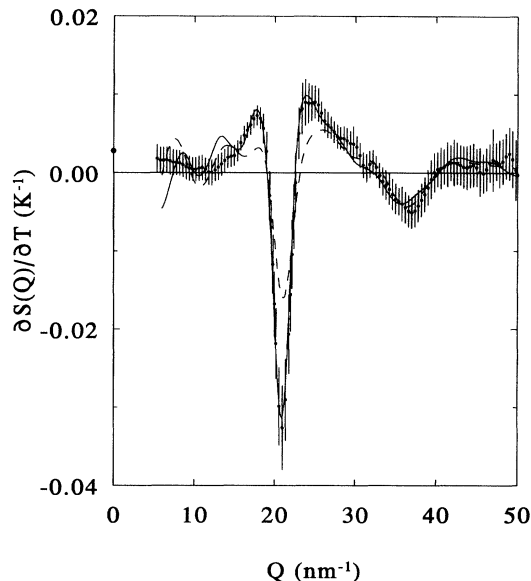


FIG. 3. Temperature derivative of the structure factor on the $n = 25.4 \text{ nm}^{-3}$ isochore evaluated at $T = 22.0$ K. The dots with the error bars are the present experimental results. The lines refer to the path integral Monte Carlo simulations, and their meaning is as in Fig. 1. The dot at $Q = 0$ is obtained from the thermodynamic equation of state. As in Fig. 2, we note the presence of spurious oscillations in the simulation results below $Q = 15 \text{ nm}^{-1}$.

a clear choice between the LJ and a more realistic phenomenological potential, the better representation of the experimental data being provided by the latter.

The thermodynamic derivatives of $S(Q)$ are important also because they carry information on the three-body correlations [20–22]. The present structural information does not suggest a strong contribution due to irreducible three-body forces, since the pair potential alone is sufficient to reproduce the experimental results.

-
- [1] F. Barocchi, P. Chieux, R. Magli, L. Reatto, and M. Tau, *Phys. Rev. Lett.* **70**, 947 (1993).
 - [2] For reviews of theoretical methods and applications see, for example, R. Evans, in *Liquids at Interfaces*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, New York, 1989); D. W. Oxtoby, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, New York, 1991).
 - [3] A. D. J. Haymet, *J. Phys. Chem.* **89**, 887 (1985).
 - [4] M. Baus, *J. Stat. Phys.* **48**, 1129 (1987).
 - [5] T. V. Ramakrishnan and M. Yussouff, *Phys. Rev. B* **19**, 2775 (1979).
 - [6] J. D. McCoy, S. W. Rick, and A. D. J. Haymet, *J. Chem. Phys.* **90**, 4622 (1989).
 - [7] D. M. Ceperley and E. L. Pollock, *Phys. Rev. Lett.* **56**, 351 (1986).
 - [8] D. G. Henshaw, *Phys. Rev.* **119**, 9 (1960).

-
- [9] E.C. Svensson, V.F. Sears, A.D.B. Woods, and P. Martel, *Phys. Rev. B* **21**, 3638 (1980).
- [10] W. Montfrooij, L.A. de Graaf, P.J. van den Bosch, A.K. Soper, and W.S. Howells, *J. Phys. Condens. Matter* **3**, 4089 (1991).
- [11] M. Zoppi, U. Bafile, R. Magli, and A.K. Soper, *Phys. Rev. E* **48**, 1000 (1993).
- [12] L.L.B. is Laboratoire Commun CEA-CNRS.
- [13] E. Guarini, F. Barocchi, R. Magli, U. Bafile, and M.C. Bellissent-Funel, *J. Chem. Phys. Condens. Matter* (to be published).
- [14] M. Zoppi, *Physica (Amsterdam)* **183B**, 235 (1993).
- [15] M.J. Norman, R.O. Watts, and U. Buck, *J. Chem. Phys.* **81**, 3500 (1984).
- [16] M. Neumann and M. Zoppi, *Phys. Rev. A* **44**, 2474 (1991).
- [17] L. Verlet, *Phys. Rev.* **165**, 201 (1968).
- [18] H.M. Roder, G.E. Childs, R.D. McCarty, and P.E. Angerhofer, NBS Technical Note No. 641, 1973 (unpublished).
- [19] R. Aziz and M.J. Slaman, *Mol. Phys.* **58**, 679 (1986).
- [20] F.P. Buff and R. Brout, *J. Chem. Phys.* **33**, 1417 (1960).
- [21] H.J. Raveché and R.D. Mountain, *J. Chem. Phys.* **57**, 3987 (1972).
- [22] P.A. Egelstaff, *Annu. Rev. Phys. Chem.* **24**, 159 (1973).