Quantum Mechanical Effects on the Static Structure Factor of Pairs of Orthodeuterium Molecules

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Neutron diffraction results on low density orthodeuterium gas at four densities along the 36.0 K isotherm are reported. The zero-density limit of the Fourier transform of the pair correlation function of this quantum mechanical system has been derived and computed both classically and quantum mechanically using a recently proposed intermolecular isotropic potential for hydrogen. The pure quantum effects on the static structure factor of the deuterium pair, mainly due to the diffraction of Boltzmann particles, have been thus measured. The comparison between experimental and theoretical results confirms the inadequacy of the classical description, while the quantum mechanical calculation gives a good account of the structural properties. [S0031-9007(98)07976-9]

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In an isotropic fluid of N spherical particles contained in a volume V at a temperature T, the pair correlation function $g(r)$ can be written as a series expansion with respect to the number density n. In particular, for sufficiently low density, only the first two terms of the series need to be retained, giving [1]

$$g(r) = g_0(r) + n g_1(r) + O(n^2), \qquad (1)$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of particles 1 and 2, $g_0(r)$ is the zero-density limit, which is completely determined by the pair interaction, while $g_1(r)$ is the three-body correlation term, which contains, in principle, also the correlation induced by the irreducible three-body interaction. Similar to Eq. (1), the quantity $H(k)$ defined as

$$H(k) = \frac{S(k) - 1}{n} = \int d\mathbf{r} \, \exp(-i\mathbf{k} \cdot \mathbf{r})[g(r) - 1], \qquad (2)$$

where $S(k)$ is the static structure factor and $\mathbf{k}$ is the wave vector, can be expanded with respect to density, i.e.,

$$H(k) = H_0(k) + n H_1(k), \qquad (3)$$

where

$$H_0(k) = \int d\mathbf{r} \, \exp(-i\mathbf{k} \cdot \mathbf{r})[g_0(r) - 1], \qquad (4)$$

$$H_1(k) = \int d\mathbf{r} \, \exp(-i\mathbf{k} \cdot \mathbf{r}) g_1(r). \qquad (5)$$

Recent large and small angle neutron diffraction experiments have permitted high precision determinations of the structure factors $S(k)$ of diluted monatomic gases, e.g., ar-

gon [2–4]. Moreover, measurements of the dependence of $S(k)$ on the density n have allowed the extraction of $H_0(k)$ and $H_1(k)$ [2,3]. In those experiments the argon gas was maintained at $T = 140$ K, therefore classical statistical mechanics applied satisfactorily for the description of the sample properties. In the classical limit $g_0(r)$ is given by $g_{cl}(r) = \exp[-\phi(r)/k_B T]$, where $\phi(r)$ is the pair interaction potential and k_B the Boltzmann constant. Hence an experimental determination of $H_0(k)$ and consequently of $g_0(r)$ gives the possibility of direct experimental determination of the pair interaction potential [2].

When the deviations from classical behavior are significant, a quantum mechanical approach has to be applied. A way of considering theoretically these effects has been presented in Ref. [5] and consists of calculating the energy eigenfunctions for the relative motion and summing the appropriately weighted probability densities over all eigenstates. In particular, for an isotropic quantum mechanical system composed of molecules with internal degrees of freedom that do not couple with the translational motion, $g_0(r)$ is given by [5]

$$g_0(r) = 4\sqrt{2}\,\lambda^3 \sum_i P_i \sum_j \Psi_j^*(r) \exp(-H/k_B T)\Psi_j(r), \qquad (6)$$

where H and $\Psi_j(r)$ are the translational Hamiltonian and translational wave function of the relative motion of the two particles, respectively, while $\lambda = h/(2\pi m k_B T)^{1/2}$ is the thermal wavelength of the molecule of mass m at the temperature T. The Boltzmann factors P_i, normalized according to $\sum_i P_i = 1$, account for the internal states of the two particles. In this case a measurement of $H_0(k)$ gives direct and relevant information on the quantum mechanical behavior of the considered pair, which is contained in the

wave function $\Psi_i(r)$. To this end, starting from Eq. (6), Ref. [5] shows that the quantum mechanical $g_0(r)$ can be written in a form which separates the quantum diffraction effects of Boltzmann particles from the quantum effect of symmetry properties, related to either Bose-Einstein or Fermi-Dirac statistics, as

$$g_0(r) = g_B(r) + g_S(r), \qquad (7)$$

where $g_B(r)$ is the Boltzmann statistics term, $g_S(r)$ contains the symmetry effects, and

$$g_B(r) = \sum_{l=0}^{\infty} g_l(r), \qquad g_S(r) = \gamma \sum_{l=0}^{\infty} (-1)^l g_l(r), \quad (8)$$

with

$$\frac{1}{2}(1 \pm \gamma) = \sum^{\pm} P_i. \qquad (9)$$

The plus and minus refer to summation over states that are symmetrical and antisymmetrical upon interchange of the two molecules, respectively. Here l is the value of the relative angular momentum of the pair, while $g_l(r)$ consists of a contribution from both the continuum and bound states of the pair, i.e.,

$$g_l(r) = (2l + 1) \frac{\sqrt{2}\,\lambda^3}{\pi^2} \int_0^{\infty} dk\, k^2 \exp\left(-\frac{\lambda^2 k^2}{2\pi}\right) |F_{kl}(r)|^2$$
$$+ (2l + 1) \frac{\sqrt{2}\,\lambda^3}{\pi^2} \sum_n^{(l)} \exp(-E_{nl}/k_B T)\, |R_{nl}(r)|^2. \qquad (10)$$

The first term in Eq. (10) is the contribution from the continuum states $F_{kl}(r)$; the second term is the contribution from the bound states $R_{nl}(r)$ of the pair, and the sum is over all the bound states of energy E_{nl} for a given value of l.

In this Letter we report the results of neutron diffraction measurements in low density gas from which the $H_0(k)$ of an interacting quantum mechanical system has been evaluated for the first time. We then compare the experimental $H_0(k)$ with the theoretical one derived by Fourier transformation of the $[g_0(r) - 1]$ calculated from Eqs. (7)–(10). The investigated quantum system is gaseous orthodeuterium at $T = 36$ K. Several reasons have motivated this choice. First, the orthodeuterium molecules in their $J = 0$ rotational state interact with an isotropic potential like atoms do, therefore the theoretical approach outlined previously applies and the states of the pair can be calculated neglecting the anisotropic potential contribution, which is small anyway. Moreover, at that temperature the symmetry $g_S(r)$ contribution to $g_0(r)$ is negligible for deuterium [5]; therefore only the quantum behavior of the Boltzmann particles is detected and studied in this case. Finally, the choice of deuterium allows a more accurate determination of $H_0(k)$ because of the favorable coherent/incoherent scattering cross section ratio with respect to hydrogen.

The neutron scattering experiment was performed at the D4B diffractometer of the Institute Laue Langevin (ILL) in Grenoble, at four densities (1.47, 1.79, 2.13, and 2.77 molecules nm^{-3}), along the (36.0 ± 0.5) K isotherm. The orthodeuterium gas was contained in a cylindrical vanadium vessel (outer radius 10 mm, wall thickness 0.2 mm, and height 70 mm) mounted on an ILL "*orange cryostat*." The equilibrium concentration of the ortho-deuterium species at 36 K is 88%, approximately, and its attainment was speeded up by the presence of a solid catalyst made of Cr_2O_3-γAl_2O_3. The temperature and pressure were measured continuously and were stable within a few parts per thousand. The incident wavelength was $\lambda_0 = 0.7037$ Å and the diffractometer was in its standard configuration, i.e., with two ^{3}He multidetectors, the first one at 1.50 m from the sample position and the second at 0.75 m. The measurements were taken in repeated runs to judge the stability of the experimental setup. The data were corrected for background, multiple scattering, attenuation effects, and incoherent and inelastic scattering following a procedure already successfully adopted in previous cases [2,6]. Also, an effective correction for replacing the nominal scattering angle by the average scattering angle was applied [2], and finally the data taken with the two detectors were matched in the overlap region. The high-k intramolecular contribution to the cross section was used for calibration purposes and then the center of mass structure factors derived. (The data analysis details will be published elsewhere.) In Fig. 1 the resulting experimental center of mass structure factors $S(k)$ for the four densities are shown. The statistical uncertainty of the final $S(k)$ was less than 0.4% for all the densities and over the entire k range investigated.
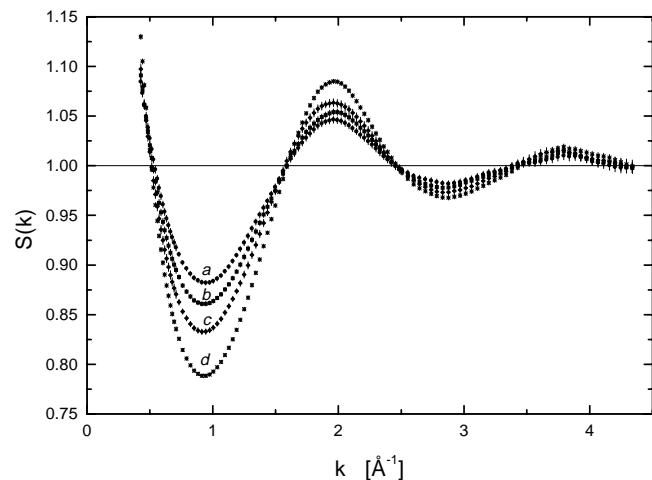

FIG. 1. Experimental center of mass static structure factors $S(k)$ of orthodeuterium at $T = 36$ K for the four investigated densities. Circles, squares, diamonds, and stars, labeled as curves a, b, c, and d, correspond to numerical densities $n = 1.47$, 1.79, 2.13, and 2.77 molecules nm^{-3}, respectively. Error bars, where not discernible, are within the symbol sizes.

The corresponding $H(k)$'s have been evaluated from Eq. (2). For each k value the $H(k)$ data showed, as a function of n, a linear behavior within the experimental uncertainties. We therefore estimated the coefficient $H_0(k)$ of Eq. (3) from a weighted, linear in the density, least-squares fit to the $H(k)$ data. The resulting $H_0(k)$ is reported in Fig. 2.

As far as the theoretical approach was concerned, the quantum mechanical calculation of $g_0(r)$ has been performed in two steps. First, the eigenfunctions were generated by numerical integration of the radial Schrödinger equation for the interacting orthodeuterium pairs, similarly to what was done in Ref. [5]. $g_0(r)$ was then calculated from Eqs. (7)–(10) using a computer code [7] and assuming, for the isotropic part of the interaction potential of orthodeuterium pairs, the empirical form given by Schaefer and Köhler [8]. The parameter γ defined in Eq. (9) assumes in orthodeuterium the value $4/9$. The chosen interaction potential has four bound states and one resonance. Estimates based on repeated calculations with varying radial grid size, free state energy increments, and truncation points of the partial wave summations, suggest that the numerical precision of the resulting radial distribution function $g_0(r)$ amounts to better than 1%. $H_0(k)$ was finally obtained by Fourier transformation of $g_0(r) - 1$.

In order to assess the importance of the quantum effects, we have calculated a classical $H_0(k)$ by Fourier transformation of $g_{cl}(r) - 1$ and by using the same pair interaction potential $\phi(r)$ [8] already chosen in the quantum calculations. Classical and quantum results for $H_0(k)$ are displayed in Fig. 2. The comparison between measured and classical results shows a significative disagreement between the two sets of data in all the explored k range, which results mainly in a phase displacement,

with the classical curve shifted towards higher k values. On the contrary, experiment and quantum results agree fairly well in almost all the investigated k range. In particular, the phase displacement between classical and quantum results shown in Fig. 2 can be interpreted qualitatively supposing that, at this temperature, the quantum effects roughly imply an enlarging of the classical molecule size by about 3%. The pure quantum mechanical response of the system, due to the wave function distribution present in Eq. (6), is shown in Fig. 3, where the difference between classical and quantum $H_0(k)$ is reported together with the corresponding difference between classical and experimental results. The two curves are in satisfactory agreement for most of the investigated k range, thus confirming the capability of the performed quantum mechanical calculation in reproducing the structural properties of deuterium. Some significant differences between experiment and quantum theory are evident only for $k < 0.5$ Å^{-1}, where $H_0(k)$ increases sharply toward the compressibility value at $k = 0$.

In conclusion, we have reported accurate experimental and theoretical determinations of the zero-density limit of the Fourier transformation of the pair distribution function of orthodeuterium at 36 K. At that temperature the quantum behavior of orthodeuterium pairs is appreciable and mainly due to the diffraction of Boltzmann particles, while symmetry effects are almost negligible. The comparison between neutron scattering data and theoretical results confirms the extent of the quantum effects and, consequently, the clear inadequacy of a classical picture to represent the structural properties of this system. Moreover, if the quantum mechanical scheme introduced in Ref. [5] for computing $g_0(r)$ and a realistic isotropic intermolecular potential are used, a satisfactory description of $H_0(k)$ is obtained, with small discrepancies showing up at the lower investigated k values. More accurate experimental and
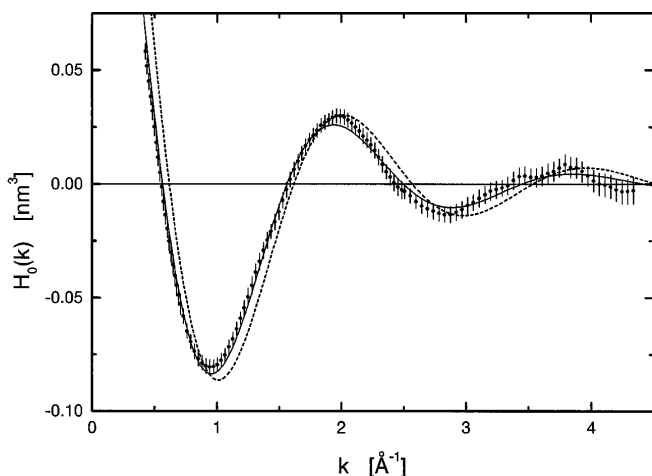

FIG. 2. $H_0(k)$ of orthodeuterium at $T = 36$ K. Circles with error bars: experimental data obtained from a weighted, linear in density, least-squares fit to the $H(k)$ data; continuous and dashed lines represent quantum mechanical and classical results (see text). The pair interaction potential of Ref. [8] has been used for the theoretical curves.
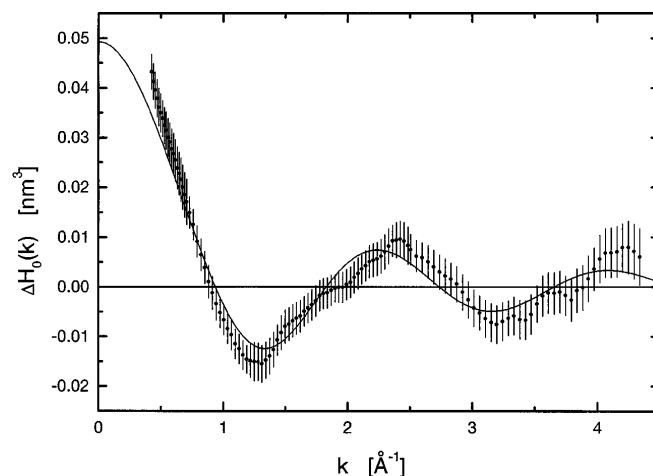

FIG. 3.   Difference between classical and experimental (circles with error bars) and classical and quantum mechanical (line) $H_0(k)$ for orthodeuterium at $T = 36$ K.

theoretical results for $k < 0.5$ Å^{-1} are required for clarifying the physical meaning of these differences.

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[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1986).

[2] H. Fredrikze, J. B. van Tricht, A. A. van Well, R. Magli, P. Chieux, and F. Barocchi, Phys. Rev. Lett. **62**, 2612 (1989).

[3] R. Magli, H. Fredrikze, P. Chieux, and F. Barocchi, Europhys. Lett. **15**, 609 (1991).

[4] R. Magli, F. Barocchi, P. Chieux, and R. Fontana, Phys. Rev. Lett. **77**, 846 (1996).

[5] J. D. Poll and M. S. Miller, J. Chem. Phys. **54**, 2673 (1971).

[6] E. Guarini, F. Barocchi, R. Magli, U. Bafile, and M. C. Bellissent-Funel, J. Phys. Condens. Matter **7**, 5777 (1995).

[7] M. Moraldi, Chem. Phys. **78**, 243 (1983); M. Moraldi, A. Borysow, and L. Frommhold, Chem. Phys. **86**, 339 (1984).

[8] J. Schaefer and W. E. Köhler, Z. Phys. D **13**, 217 (1989).