Short-range order in liquid deuterium under pressure

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The structure factor of liquid ortho-deuterium was investigated by neutron diffraction all the way to 25 Å^{-1} for three densities: near the melting curve at pressures 3.6 and 900 bar and in the vicinity of the critical point. The contributions of the intra- and intermolecular correlations are separated, and the radial distribution functions in the liquid and the short-range order structure parameters are separated. It is shown that the change of the liquid-deuterium density near the melting curve under pressure is due to the change of the mean distances between the molecules, whereas in the critical region the principal effect is the decrease of the mean number of nearest neighbors. In contrast to recent suggestions [M. J. Clouter, C. G. Deacon, and H. Kiefle, Phys. Rev. Lett. **58**, 1116 (1987)], liquid molecular deuterium behaves in the critical region as a simple liquid.

1. INTRODUCTION

Liquid hydrogen and deuterium find various and important uses in research and energy programs, and their physical properties are therefore extensively investigated. Nonetheless, important information such as structure data on the short-range order in these cryogenic liquids has not been heretofore available. From the standpoint of liquid-state physics, these systems are of interest as the simplest molecular liquids with predominantly central interaction, in which quantum properties can be manifested as a result of the weak-molecular bond and the low mass.

The structure factor of a liquid can usually be obtained from x-ray or neutron diffraction experiments. Liquid hydrogen, however, poses certain difficulties. Hydrogen has too low a scattering ability for x-ray investigations, and to large an incoherent background and scattering recoil for neutron investigations. Conditions are more favorable for the observation of coherent effects in neutron scattering by deuterium, although even here the difficulty of correcting for inelastic scattering is appreciable.

We report here the results of neutron-structure investigations of liquid ortho-deuterium. Ortho-deuterium with a molecule spin $I = 0$ or 2 and with a rotational quantum number $J = 0$ is a thermodynamically stable modification of molecular deuterium at low temperatures, characterized by an isotropic intermolecular interaction. To investigate the short-range order in the liquid in a wide range of densities, the measurements of ortho-deuterium structure factor were undertaken at low and high (about 1 kbar) pressures near the critical point.

2. EXPERIMENTAL DETAILS

The structure investigations were carried out with the pulsed slow-neutron source of the "Fakel" accelerator (Kurchatov Atomic-Energy Institute). Time-of-flight measurements were made with a multidetector neutron diffractometer, using a high-pressure gas facility. The experimental procedure was similar in many respect to that previously used in studies of solid hydrogen and deuterium,[1,2] except for some details.

Pure ortho-deuterium was obtained by thermosorption from $(LaNi_5)D_6$, kept at $T = 20$ K in a para-ortho converter with an $Fe(OH)_3$ catalyst, and condensed in a pressure chamber located in a helium cryostat. The chamber temperature was regulated by pumping on helium vapor and by a heater. The deuterium gas pressure was produced by an external compressor and transmitted by a capillary to the chamber with the liquid sample.

To decrease the background, the pressure chamber (inside diameter 1.8 cm, height 6 cm, and wall thickness 0.5 cm) was made of $Ti_{67.5}Zr_{32.5}$ alloy—"zero" matrix for coherent neutron scattering, and a scattered-radiation collimator in the diffractometer limited precisely the sample-detector solid angle. This made it possible to exclude completely the background of coherent reflections from the chamber and cryostat materials for 14 detectors placed in a scattering-angle range $2\theta = 22–135°$. It was therefore possible to measure the pattern of neutron-diffraction from liquid deuterium in a rather large range of momentum transfer Q, from 0.8 to 25 Å^{-1}. The neutron transmission through the chamber with the sample could be measured simultaneously. This made possible an independent determination of the liquid-deuterium density at various pressures and temperatures.

3. DATA REDUCTION

When determining the structure factor $S(Q)$ of a liquid consisting of molecules, it is convenient to separate the intra- and intermolecular correlations[3]:

$$S(Q)=f_1(Q)+f_2(Q)\,[S_c(Q)-1], \tag{1}$$

where Q is the momentum transferred by neutron scattering; $f_1(Q)$ is the form factor of one molecule, determined by the positions of the nuclei inside the molecules; f_2 is a form factor that takes into account the possible orientational correlations between the molecules; $S_s(Q)$ is the structure factor for the molecule centers.

For liquid ortho-deuterium we have

$$f_1(Q)=1+\sin(Qa)/Qa, \tag{2}$$

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where a is the distance between the deuteron in the rigid D_2 molecule; $f_2(Q) = 1$ as a result of the isotropy of the intermolecular interaction, and

$$S(Q)=\sin(Qa)/Qa+S_c(Q). \tag{3}$$

The structure factor was determined by reducing the experimental data on the basis of the following relation:

$$N\frac{I_{s,c}-\tilde{I}_c}{\tilde{I}_{v,a}-\tilde{I}_a}\frac{A_sA_cM_s}{A_vM_v}\frac{\sigma_s^{v}}{4\pi}P_v=\frac{\sigma_s^{s}}{4\pi}P_s+\langle b\rangle^2[S(Q)-1], \tag{4}$$

where $I_i = I_i^{\theta}(t)$ is the normalized neutron-scattering intensity determined by measuring the time of flight t for the scattering angle 2θ. The subscript i numbers one of four independent-measurements; s and c designate neutron scattering by the investigated sample (s) in the chamber (c), c is the background from the empty chamber, v is neutron scattering by a standard vanadium sample (determination of the shape of the neutron spectrum), a is the background due to scattering by air; the tilde denotes mathematical smoothening of the measured spectrum to reduce the statistical spread of the data; A_i. M_i, and P_i are corrections for absorption,[4] multiple[5] and inelastic[6] neutron scattering, respectively, and depend respectively on t, θ, and the experimental geometry (for a useful summary of equations see, e.g., Ref. 7);

$$Q=\gamma Q_e=\gamma\frac{4\pi}{h}m\frac{(L+l)}{t}\sin\theta;$$

L and l are the source-sample and sample-detector flight lengths, respectively; m is the neutron mass; γ is a factor that takes the recoil effect in quasielastic scattering (see below); N is a normalization coefficient determined from the condition that $S(Q_{\max}) = 1$ at a certain sufficiently large $Q = Q_{\max}$; σ_s^s and σ_s^x are the total cross sections for neutron scattering by the sample and by vanadium, respectively; $\langle b\rangle$ is the amplitude, averaged over the spins, of the coherent neutron-deuteron scattering.

The D_2-molecule mass ($M = 4$) is comparable with the neutron mass ($m = 1$), so that the corrections for inelastic scattering and for the recoil effect in the lab are quite substantial. They were taken into account in the form of a Placek correction[6] to the proper part $P_s(Q)$ of the scattering and in the change of the momentum-transfer scale $\gamma = Q/Q_e$.[7,8] The corresponding equations[7] follow:

$$P_s(Q)=1-\alpha\frac{m}{M^*}\sin^2\theta\cdot B+\frac{m}{M^*}\frac{kT}{2E}[\cos 2\theta-C], \tag{5}$$

where $\alpha = 2$ for a detector with efficiency proportional to t; M^* is the effective mass of the scatterer; E is the neutron energy;

$$B=[1-f(1-2\eta)]+\frac{m}{M^*}[1-f(1-2\eta)(1+2\eta f)\sin^2\theta];$$

$$C=2f(1+2\eta)[1-2f(1+\eta)\sin^2\theta];$$

$\eta = -\partial\ln\Phi(E)/\partial\ln E$ is the characteristic of neutron spectrum $\Phi(E)$; $f = l/(L+l)$ is a parameter indicative of the ratio of the flight lengths before and after the scattering,

$$\gamma=\frac{Q}{Q_e}=\frac{(f/x+1-2f)}{2(1-f)}\frac{(1+x^2-2x\cos 2\theta)^{1/2}}{\sin\theta}, \tag{6}$$

where

$$x^2=1-2\frac{m}{M^*}\frac{1}{(1+m/M^*)^2}\left[1-\cos\left(2\theta+\arcsin\left(\frac{m}{M^*}\sin 2\theta\right)\right)\right].$$

Two factors have decreased somewhat these corrections under the conditions of this experiment: the relatively low liquid-deuterium temperature ($T\approx 20$–40 K) compared with characteristic neutron energies ($E\gtrsim 300$ K), and the low flight length l after the scattering (the parameter $f = 4.7\cdot 10^{-2}$). The principal uncertainty, however, remained the choice of the effective scatterer mass M^* for liquid molecular deuterium. We have regarded this quantity as a fit parameter chosen from the condition that the structure factors $S^{\theta}(Q)$ calculated from independent measurements at different scattering angles 2θ coincide in overlapping Q regions. The effective mass M^* estimated in this manner for liquid deuterium was found to equal 5.3. As a result, the structure factor $S(Q)$ was obtained by averaging 14 independently reduced $S^{\theta}(q)$ spectra.

The reduced $G(r)$ and total $RDF(r)$ radial-distribution functions of the nuclei in liquid deuterium were calculated from $S(Q)$ by using the fast-Fourier-transform algorithm:

$$G(r)=\frac{2}{\pi}\int_0^{Q_{max}}Q[S(Q)-1]\sin Qr\cdot M(Q)\,dQ, \tag{7}$$

$$RDF(r)=4\pi r^2\rho_0+rG(r), \tag{8}$$

$$M(Q)=\frac{Q_{max}}{\pi Q}\sin\pi Q/Q_{max}$$

is called the modification function for decreasing the contribution of false oscillations arising in Fourier inversion due to the finite integration limit $Q_{\max}$, and ρ_0 is the macroscopic density of liquid deuterium.

$G(r)$ yields the most probable distances R_n between the nearest molecules in the liquid and the half-widths Δ_n of the spatial distributions, while $RDF(r)$ yields the coordination numbers

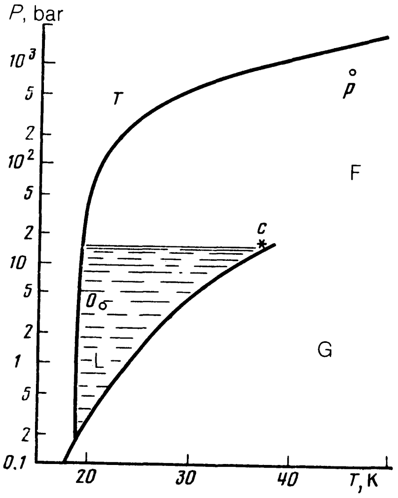

FIG. 1. P–T diagram of deuterium: G—gas, F—fluid, L—liquid, T—solid. The points mark the pressures and temperatures at which the neutron-diffraction measurements were made.

TABLE I. Close-order structure parameters in liquid ortho-deuterium at various densities (P, 0, C)

	P	0	c *
V (cm^3/mol)	20.7	23,5	59,0
P (bar)	900	3.6	16.7
T (K)	46	21,5	37,5
R_1 (Å)	3.45(2)	3,63(2)	3,84(7)
Δ_1 (Å)	1,19(5)	1,25(5)	1.40(9)
Z_1	13,3(2)	13,3(2)	6,6(5)
R_2/R_1	1,81(2)	1,80(2)	1.78(4)
R_3/R_1	2.64(3)	2.62(3)	2,60(7)

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*The critical-point parameters are $P_{cr} = 16.65$ bar, $T_{cr} = 38.26$ K, $V_{cr} = 59.9$ cm^3/mol.

$$Z_n = \int_{r^n_{\min}}^{r^n_{\max}} RDF(r)\,dr \tag{9}$$

($r^n_{\min}$ and $r^n_{\max}$ are the boundaries of the n-coordination medium).

4. RESULTS AND THEIR DISCUSSION

The structure factor of ortho-deuterium was investigated at low (0) and high (p) pressures in the liquid and fluid phases not far from the melting curve, and also near the critical point (c), where its specific volumes differ substantially: $V_p = 20.7$; $V_0 = 23.5$ and $V_c = 59.0$ cm^3/mol. The corresponding thermodynamic parameters are marked on the P–T diagram (Fig. 1) and are listed in Table I.

The $S(Q)$ measured at various densities are shown in Fig. 2. Manifestations of inter- and intramolecular correlations in the structure factor are visible. The intensities and positions of the first two peaks change noticeably with density at small Q, a manifestation of close-order correlation between the molecules and the liquid. For large Q, the form of the structure factor is independent of pressure and temperature, and agrees with the behavior (2) typical of a two-atom molecule.

Figure 3 shows the functions $G(r)$ that are indicative of the radial distribution of nuclei in liquid deuterium at three values of its density. They were obtained by taking Fourier transforms of $S(Q)$ up to $Q_{\max} = 23$ Å^{-1}. The first narrow peak observed in all three distributions at $R_0 = (0.74 \pm 0.02)$ Å corresponds to a distance $a = 0.742$ Å between the deuterons in a free D_2 molecule. Its half-width Δ_0 is determined entirely by the resolution of the Fourier transform:

$$\Delta_0 = \Delta_{FT} = 5.44/Q_{max} = 0.24 \text{ Å}, \tag{10}$$

and the integral yields for the coordination number a value $Z_0 = 1.0 \pm 0.2$, just as for a two-atom molecule. All this is evidence that on condensation into a liquid the D_2 molecules, as expected, retain their rigidity. On the other hand, the equality of the results for the intramolecular structure from measurements at different densities can attest to a correct introduction of the corrections in the reduction of the experimental data.

Intermolecular correlations that determine the short-range order in a liquid are manifested by broad oscillations of the $G(r)$ distribution, which depend on the density and attenuate rapidly with distance. Local fluctuations of the nuclear density about its mean value are noticeable in liquid

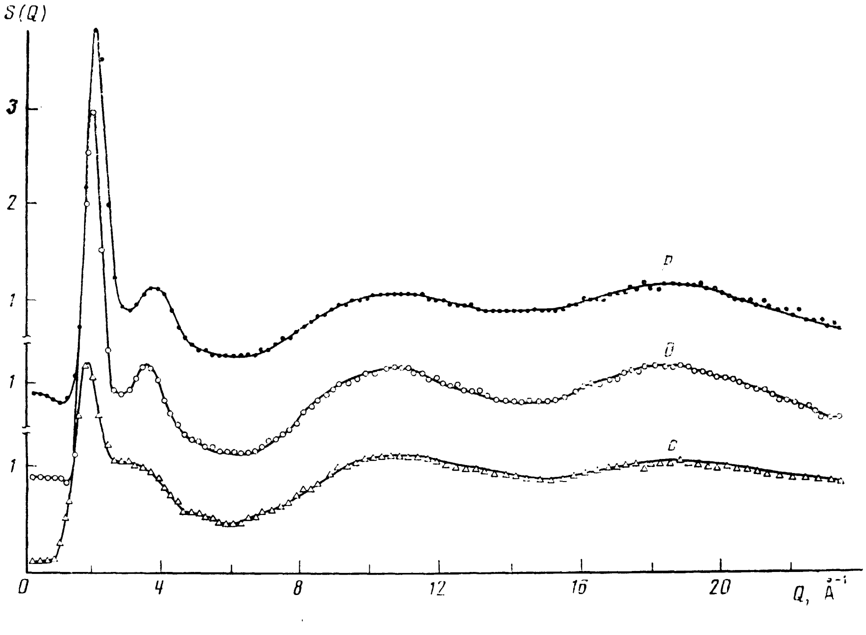

FIG. 2. Structure factor $S(Q)$ of liquid ortho-deuterium under pressure near the melting curve ($0, p$) and near the critical-point (c): p—$V = 20.7$ cm^3/mol, 0—23.5 cm^3/mol, C—59.0 cm^3/mol.

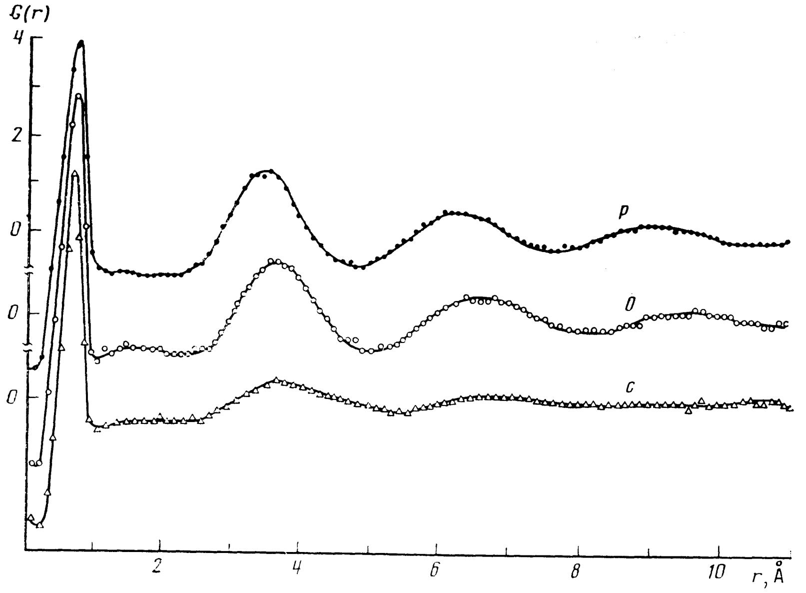

FIG. 3. Reduced radial-distribution function $G(r)$ in liquid deuterium near the melting curve (p, 0) and near the critical point (c). See Fig. 2 for the notation.

deuterium up to distances ~10 Å. The minimum distance $r_{\min}$ at which a deuteron of a neighboring molecule is observable turns out to be the same, (2.57 ± 0.03) Å, in all three cases. This yields an estimate of the "diameter" of the rigid D_1 molecule:

$$d = r_{min} + a = (3.31 \pm 0.03)\ \text{Å}. \qquad (11)$$

Note that this value corresponds to the position of the minimum of the Lennard-Jones potential for gaseous deuterium.

The structural parameters that characterize the short-range order in liquid deuterium at various densities are listed in Table I. In the calculations of the coordination numbers Z_1, the lower limit $r^1_{\min}$ corresponded to 2.6 Å, and the upper limit $r^1_{\max}$ was chosen to be 4.8, 5.0, and 5.4 Å for the densities p, 0, and c, respectively. On compression of liquid deuterium close to the melting curve, the most probable distances r_1 between neighboring molecules decrease with increase of the density. The average coordinate number Z_1 describing the nearest surround remains in this case close to 13.6, which is typical of random close-packing simulation.[10] The relative peak positions of the molecule radial distribution in liquid deterium are independent of the density. The ratios are $R_2/R_1 = 1.8$ and $R_3/R_1 = 2.6$, in good agreement with model of random close packing of spheres and with the experimental data for simple monatomic liquids.[10]

On going over to the critical point, where the deuterium density is decreased to approximately one-third, the change of the mean distances between molecules is not as large—by less than 10%. At the same time, the amplitude of the oscillations in $G^c(R)$ decreases substantially, the dispersion (half-width Δ^c_1) of the spatial distribution increases, and the average number Z^c_1 of the nearest neighbors decreases noticeably. The main effect of the deuterium-density change in the critical region is thus due to formation of voids in the short-range order.

The behavior of deuterium in the vicinity of the critical point has attracted particular interest in view of recent suppositions based on optical-spectroscopy results.[11] With approach to the critical region, the appearance of a fine structure has been observed in the Raman spectra of the intramolecular oscillations of D_2 (but not H_2 or HD), and interpreted as enhancement of the local ordering in the deuterium fluid in the critical region. Direct neutron-structure investigations in the immediate vicinity of the critical point, however, do not confirm this supposition. In many respect, liquid molecular deuterium behaves as a simple liquid.

5. CONCLUSION

Investigations of the short-range order in the liquid and fluid phases of ortho-deuterium have shown that the change of its density under pressure near the melting point is due to change of the average distances between the molecules, with preservation of a nearest surround typical of dense random close packing. In the critical region, the main effect of the density change is formation of voids (vacancies) in the short-range order.

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