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Abstract. We measured the static structure factor $S(k)$ of dense fluid helium by neutron diffraction as a function of density (at fixed temperature $T = 13.3$ K) and as a function of temperature (at fixed number density $n = 18.7$ nm^{-3}). We give the results and calculate the density derivative at $T = 13.3$ K; $n = 22.0$ nm^{-3}. We use this density derivative, which is determined by the triplet correlation function $g_3(r, s)$, to test the proposal for $g_3(r, s)$ made by Winfield and Egelstaff. We find that this proposed form of $g_3(r, s)$ gives a reasonable prediction for our experimental derivative. Hence, we use this proposal to estimate the square of the energy-density correlation function at equal times, $l^2(k)$, from our experiments, using the temperature derivative at $n = 18.7$ nm^{-3} and $T = 13.3$ K.

1. Introduction

In the theory of simple liquids there exist numerous examples in which correlation functions of more than two particles play an important role in the macroscopic properties of a liquid, such as in calculating the energy of a system (Barker *et al* 1971). The pair correlation function $g(r)$ can be determined directly by means of x-ray experiments or by neutron diffraction. One then measures the Fourier transform $S(k)$ of the pair correlation function, given by

$$S(k) = \frac{1}{N}\left\langle \sum_{i,j}^{N} e^{ik\cdot(r_i - r_j)} \right\rangle = 1 + n \int_V dr\, e^{ik\cdot r}[g(r) - 1] \qquad (1.1)$$

in which r_i denotes the position of particle i, N is the total number of particles in a volume V, $k = |k|$ is the Fourier wavenumber, the brackets denote the canonical ensemble average and $n = N/V$ is the number density.

Higher order correlation functions, like the triplet correlation function $g_3(r, s)$, cannot be determined directly. However, by measuring the temperature and density dependence of the pair correlation function $g(r)$ (or equivalently the static structure factor $S(k)$) one can get indirect information on higher order correlation functions because the derivatives are determined by these higher order functions.

We have carried out five diffraction experiments on helium and calculated the density and temperature derivatives of the static structure factor. We use these derivatives to

Table 1. Thermodynamic (n, p, T) states of helium for which $S(k)$ is measured.

n (nm^{-3})	T (K) 4.29	13.3	21.89
18.7	1.12 bar	40.3 bar	78.4 bar
22.0	—	58.3 bar	—
24.8	—	81.6 bar	—

Table 2. Merge parameters used in the diffraction experiments at ISIS.

Det. angle	$\Delta k/k$ %	k nm^{-1}	E_0 meV	λ_0 nm
4.8°	11	1–12	3.0–425	0.53–0.044
9.6°	6	4–25	12.1–470	0.26–0.042
20.5°	2.8	9–50	10.8–421	0.28–0.044
35.3°	1.7	30–80	51.5–366	0.13–0.047

test a model for the triplet correlation function and to estimate the energy-density correlation function at equal times.

The organization of this paper is as follows. In section 2 we describe the experiments and show the $S(k)$, in section 3 we discuss the density derivative of $S(k)$ and compare it with the model for $g_3(r, s)$ as proposed by Winfield and Egelstaff (Winfield and Egelstaff 1973). In section 4 we discuss the temperature derivative and use the Winfield–Egelstaff model to calculate the energy-density correlation function at equal times.

2. Experiment

The experiments were carried out at the Rutherford Appleton Laboratory using the time-of-flight (TOF) diffractometer LAD. We measured the structure factor $S(k)$ of helium for five thermodynamic states, which are listed in table 1†.

For our experiments we used a sample container which consisted of a single vanadium cylinder of height 5 cm, diameter 2 cm and wall thickness 0.05 cm (Zoppi *et al* 1989). The cross section of the incident beam was 1.5×4.0 cm^2. To avoid large inelasticity corrections, only the detector groups at small scattering angles (5, 10, 20 and 35°) were used. The static structure factors $S(k)$ were calculated from the TOF spectra using the LAD standard correction programs (Soper *et al* 1989). These programs correct the neutron spectra for background and multiple scattering, carry out absorption and inelasticity corrections and normalize the spectra to a vanadium standard. Finally, the results of all the detector groups are merged to produce a single $S(k)$. The relevant parameters for this last step are listed in table 2, in which E_0 and λ_0 denote the energy and wavelength range of the scattered neutrons, respectively. We note that the multiple scattering

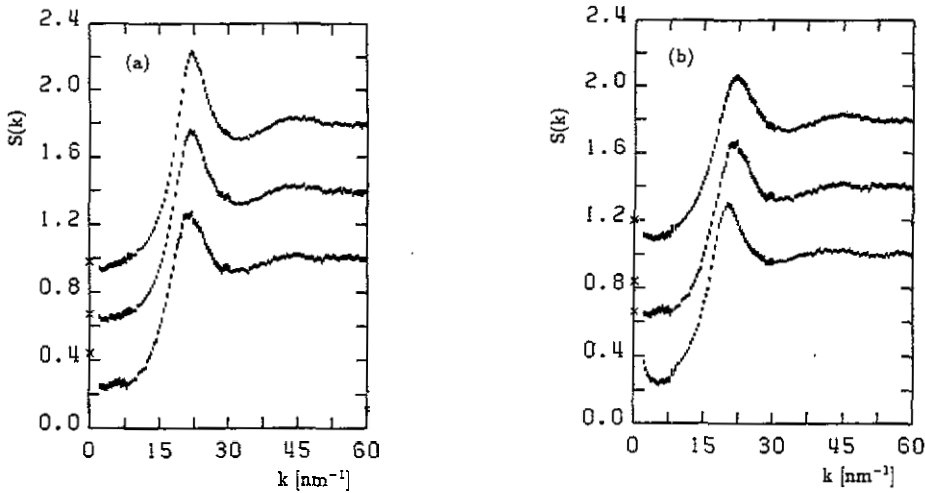† A tabulated version of $S(k)$ is available upon request.

Figure 1. (*a*) The measured static structure factor $S(k)$ as a function of the number density n at constant temperature $T = 13.3 \, \text{K}$ (top: $n = 24.8 \, \text{nm}^{-3} (S(k) + 0.8)$, middle: $n = 22.0 \, \text{nm}^{-3}$ $(S(k) + 0.4)$, bottom: $n = 18.7 \, \text{nm}^{-3}$). (*b*) The measured static structure factor $S(k)$ as a function of the temperature T at constant number density $n = 18.7 \, \text{nm}^{-3}$ (top: $T = 21.9 \, \text{K}$ $(S(k) + 0.8)$, middle: $T = 13.3 \, \text{K}$ $(S(k) + 0.4)$, bottom: $T = 4.3 \, \text{K}$). The $S(0)$ values (crosses) are obtained from independent thermodynamic compressibility data (Sychev *et al* 1987)

correction is of the order of a few percent because of the small scattering cross section of the helium atoms. The average scattering fraction of our sample was 5%.

We plot the structure factors $S(k)$ as a function of density (figure 1(*a*)) and as a function of temperature (figure 1(*b*)) for wavenumbers k up to 60 nm^{-1}. One can see from this figure that there is a shift in peak position when the density or temperature is varied. This is as expected because the effective particle diameter σ increases when the density and/or temperature is lowered and the peak position of $S(k)$ is roughly given by $k\sigma \approx 2\pi$. Furthermore, the increase of σ with decreasing temperature is enhanced by the quantum nature of the light helium atoms (the helium atom is less sharply defined at lower temperatures, resulting in a larger effective diameter).

To check our data, we compare the $S(k)$ at 4.29 K and SVP with the $S(k)$ measured by Svensson and coworkers (Svensson *et al* 1980) for (almost) the same thermodynamic state (4.27 K) and SVP) in figure 2. It can be seen in this figure that the two data sets almost coincide. The k resolution at $k = 20 \, \text{nm}^{-1}$ is 0.5 nm^{-1}. The points at $k = 0$ are taken from independent thermodynamic data (Sychev *et al* 1987) according to

$$S(0) = n k_{\text{B}} T \chi_T = \gamma k_{\text{B}} T / m c^2 \tag{2.1}$$

with n the number density, χ_T the isothermal compressibility, k_{B} Boltzmann's constant, T the temperature of the fluid, m the mass of a helium atom, c the adiabatic speed of sound and $\gamma = c_p/c_V$ the ratio of specific heats (c_p and c_V denote the specific heats at constant pressure and at constant volume, respectively). We now proceed with a discussion of the density derivative of $S(k)$ at $T = 13.3 \, \text{K}$ and $n = 22.0 \, \text{nm}^{-3}$.
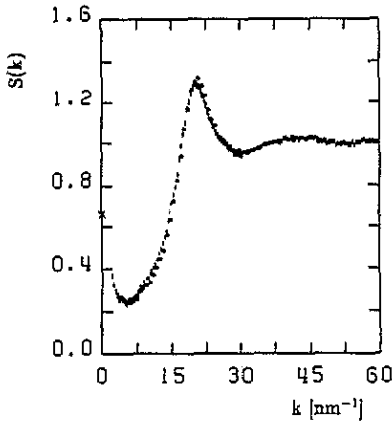
Figure 2. Comparison of the experimentally obtained $S(k)$ at 4.29 K and SVP (errorbars) with the $S(k)$ measured by Svensson and coworkers at 4.27 K and SVP (Svensson *et al* 1980) (dots).
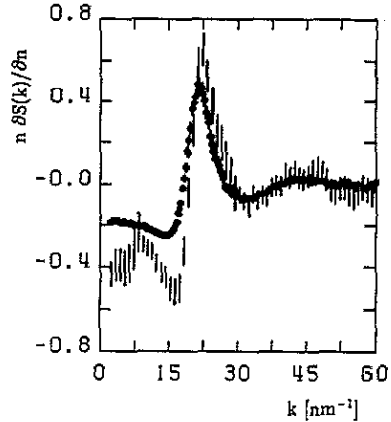
Figure 3. The experimental density derivative of $S(k)$ at constant temperature $T = 13.3$ K (number density $n = 22.0$ nm^{-3}) (crosses) compared with approximation (3.7) from the text (dots).

3. The density derivative

To determine the density derivative of $S(k)$ we use the three data sets at 13.3 K. We have calculated the derivative at $n = 22.0$ nm^{-3} by simple numerical differentiation according to

$$(\partial S(k)/\partial n)|_{T=13.3K} = \tfrac{1}{2}[S(k,n_2) - S(k,n_1)]/(n_2 - n_1) + \tfrac{1}{2}[S(k,n_3) - S(k,n_2)]/(n_3 - n_2)$$

(3.1)

with $n_1 = 18.7$ nm^{-3}, $n_2 = 22.0$ nm^{-3} and $n_3 = 24.8$ nm^{-3}. The density derivative obtained is plotted in figure 3.

We now compare this derivative with predictions based upon an expansion of the triplet correlation function $g_3(r, s)$ in terms of the pair correlation functions, the so called 'convolution approximation' (Feenberg 1969). We will follow the line as set out by Egelstaff (1973). We remark that the following expansion is valid for a classical system and could well fail at very low temperatures.

The density derivative of the pair correlation function $g(r)$ is given (exactly) by (Gubbins *et al* 1978)

$$nS(0) \frac{\partial g(r)}{\partial n}\bigg| = n \int_V [g_3(r, s) - g(r)]\, ds + 2[1 - S(0)]g(r)$$

(3.2)

where g_3 is defined analogously to $g(r)$ as

$$g_3(r, s) = \frac{1}{n^3} \bigg\langle \sum\sum\sum_{i \neq j \neq k} \delta(r_i)\delta(r - r_j)\delta(s - r_k) \bigg\rangle.$$

(3.3)

A formally exact relation expresses g_3 again in terms of g,

$$g_3(r, s) = g(r)g(s)g(r - s) \exp[\tau(r, s, |r - s|; n)].$$

(3.4)

The expansion of $g_3(r, s)$ we use is based upon the theoretical result of Abe (1959) who

has expanded (3.4) using

$$\tau(r, s, |r - s|; n) = n \int_V h(w)h(r - w)h(w - s)\, dw + O(h^4) \tag{3.5}$$

with $h(r) = g(r) - 1$.

Expanding the exponent in (3.4) we obtain (Egelstaff 1973)

$$g_3(r, s) = 1 + h(r) + h(s) + h(r - s)$$

$$+ h(r)h(s) + h(s)h(r - s) + h(r - s)h(r)$$

$$+ n \int_V h(w)h(r - w)h(s - w)\, dw + O(h^3) \tag{3.6}$$

which leads to the following equation for the density derivative of the structure factor (using all the lines of (3.6))

$$S(0)n(\partial S(k)/\partial n)|_T \approx S(0)S(k)(S(k) - 1). \tag{3.7}$$

Equation (3.7) has been applied to the structure factors of Kr (reduced density $n^* = n\sigma^3 \approx 0.2$ at $T/T_c = 1.0$) (Winfield and Egelstaff 1973), and of Ar ($n^* \approx 0.8$) (Verkerk 1985) and Ne ($n^* \approx 0.75$) (Egelstaff 1973, Verkerk 1985) both at $T/T_c = 0.8$, with T_c the critical temperature. For the low density Kr case, (3.7) gave a reasonably good approximation. However, for Ar and Ne, only a (weak) qualitative agreement was observed between the data and the prediction of (3.7), albeit that the inclusion of the subsequent lines of (3.6) gradually improved the result.

We have applied approximation (3.7) to our helium data at intermediate densities ($n^* \sim 0.5$; $T \approx 2.5T_c$) and we plot the result in figure 3. It can be seen from this figure that (3.7) not only holds qualitatively for helium, but (semi-) quantitatively as well. So apparently, triplet correlation functions do play a role in He well above the critical temperature and are well described, at the intermediate density considered in this paper, by (3.7) which is an expansion in the density. A comparison with the (real-space) results for the density derivatives in liquid helium close to the lambda transition (Raveché and Mountain 1974, Mozer *et al* 1974) remains to be done.

We end this section with two remarks. First, an equivalent way to express (3.7) is by stating that the Fourier transform $C(k)$ of the direct density correlation function is independent of the density, i.e. $\partial C(k)/\partial n = 0$, with $C(k) * S(k) = (S(k) - 1)/n$ (Fredrikze 1985). The symbol '*' denotes the convolution product.

Second, (3.6) can be generalized up to $O(h^4)$ by including the term $h(r)h(s)h(r - s)$. Equation (3.7) then reads

$$S(0)n(\partial S(k)/\partial n)|_T \approx S(0)S(k)(S(k) - 1) + (1/n)(S(k) - 1) * (S(k) - 1)^2. \tag{3.8}$$

We carried out the convolution integral numerically for our experiment, which could easily be done as a result of the accuracy of the present experiments. We find that this extra term is larger, by a factor of 100, than the first term on the right-hand side of (3.8). Such large discrepancies have also been found in related work (Haffmans *et al* 1988). We therefore conclude that although (3.7) seems to work properly in the case of our helium experiments, it is by no means certain that the expansion in powers of h (see (3.5)) can be extended straightforwardly to higher powers of h. A regrouping of higher order terms might prove to be essential in obtaining meaningful results.

We now turn to a discussion of the temperature derivative of helium at 13.3 K and 18.7 nm^{-3}.

4. The temperature derivative

We have calculated the temperature derivative at $T = 13.3$ K and $n = 18.7$ nm^{-3} by numerical differentiation using the three data sets at $n = 18.7$ nm^{-3} in analogy to the determination of the density derivative (see (3.1)). We plot the temperature derivative at constant density in figure 4.

As in section 3, we will follow the lines as set out by Egelstaff. Egelstaff has pointed out that when (3.7) is valid, one can use the temperature derivative to determine the energy-density correlation function at equal times, $l(r)$, from the experiment. Egelstaff therefore reduced the general expression for $\partial S(k)/\partial T$ at constant pressure to the following (Egelstaff 1973):

$$T(\partial S(k)/\partial T)|_p \approx (\bar{E}/nk_B T)(l^2(k) - S^2(k)) - T\alpha S(k)(S(k) - 1). \tag{4.1}$$

Here α denotes the thermal expansion coefficient and $l(k)$ is the Fourier transform of $l(r)$.

$$l(k) = 1 + n \int_V (l(r) - 1) \exp(ik \cdot r)\, dr \tag{4.2}$$

$l(r)$ is the correlation function between the local energy and local density at equal times given by

$$l(r) = \langle E(r)n(0) \rangle / \bar{E}n$$

where

$$\bar{E} = \frac{1}{V} \int_V E(r)\, dr \qquad n(r) = \sum_{i=1}^{N} \delta(r - r_i)$$

and $E(r)$ is the sum of the local kinetic and potential energy density.

Equation (4.1) is derived in a manner similar to the derivation of (3.7). However, this time not only has the triplet density correlation function, $g_3(r, s)$, been expanded according to (3.6), but the triplet energy-density correlation function, $l_3(r, s)$, has been expanded as well. Then, using all three lines of (3.6) for both $g_3(r, s)$ and $l_3(r, s)$, one obtains (4.1) (Egelstaff 1973).

Since the temperature derivative at constant pressure, p, in (4.1) is related to the temperature derivative at constant density via the density derivative at constant temperature according to

$$\frac{\partial S(k)}{\partial T}\bigg|_p = \frac{\partial S(k)}{\partial T}\bigg|_n + \frac{\partial S(k)}{\partial n}\bigg|_T \frac{\partial n}{\partial T}\bigg|_p \tag{4.3}$$

$$\approx \frac{\Delta S(k)}{\Delta T}\bigg|_n + \frac{\Delta S(k)}{\Delta n}\bigg|_T \frac{\partial n}{\partial T}\bigg|_p. \tag{4.4}$$

We can use (4.1) and (4.3) to determine the difference $l^2(k) - S^2(k)$ directly from our experiment. One can immediately see by comparing (4.1) and (4.3) that the second term on the right-hand side of (4.1) is nothing more than approximation (3.7) for the density derivative at constant pressure. Therefore, the first term on the right-hand side of (4.1) is an approximation for the temperature derivative at constant density. The amplitude of the temperature derivative at constant density is quite small (see figure 4) and the average energy per particle is 16.7 K (Sychev *et al* 1987), so the maximum difference between $l^2(k)$ and $S^2(k)$ is less than 0.1, or $l^2(k) \approx S^2(k)$.
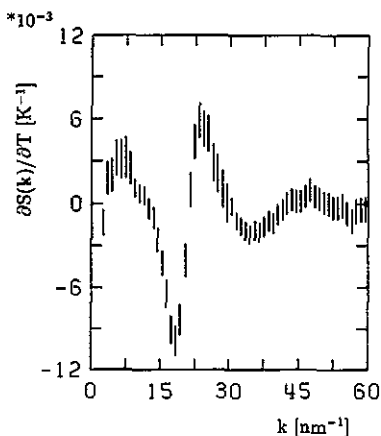
Figure 4. The experimental temperature derivative of $S(k)$ at constant number density $n = 18.7$ nm^{-3} and temperature $T = 13.3$ K.
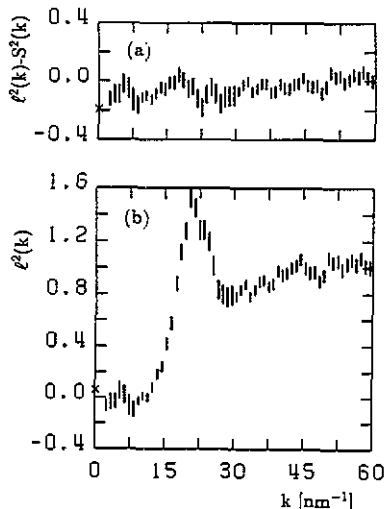

Figure 5. (a) the difference $l^2(k) - S^2(k)$ and (b) $l^2(k)$ obtained from experiment. The values $l^2(0) - S^2(0)$ and $l^2(0)$ (both denoted by crosses) in (a) and (b), respectively, are obtained from independent thermodynamic data.

The fact that $l^2(k)$ and $S^2(k)$ are very much alike can easily be understood. Since the kinetic energy is the major contribution to the total energy ($E_{kin} = 20$ K per particle, $E_{total} = 16.7$ K per particle), the peaks in the energy-density correlation function and in the density-density correlation function almost coincide and both functions are normalized to unity for large k. So, approximation (4.1) gives a result for $l^2(k)$ in accordance with what one would expect.

Finally, we wish to point out that in determining $l^2(k)$ directly from experiment it is better to perform measurements at constant density than at constant pressure. To do so, we first calculate the temperature derivative at constant pressure using (4.4) with $(\delta n/\delta T)|_{p=40.3\text{bar}} = -1.06$ nm^{-3} K^{-1} (Sychev *et al* 1987). Then we use this derivative together with (4.1) to determine the function $l^2(k) - S^2(k)$. We plot this result in figure 5 (a). Figure 5 (a) should in principle be the same as figure 4 within a constant factor. However, the two figures differ due to the use of approximation (3.7) instead of the true density derivative. Although (3.7) is a quite good approximation, it leads to unnecessary errors in $l^2(k)$, especially at low wavenumbers. This is plotted in figure 5 (b). Instead of being almost equal to $S^2(k)$, $l^2(k)$ is negative for a few k values in the low-k region. The value of $l^2(k)$ at $k = 0$ is calculated to be 0.063 using the exact relation

$$l(0) = S(0) + (1/E)(pS(0) - nk_B T^2 \alpha). \tag{4.5}$$

Therefore, if the aim is to determine $l^2(k)$ from neutron scattering experiments, it is advisable to measure at constant density instead of constant pressure.

Acknowledgment

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