Static structure of dense krypton and interatomic interaction

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Abstract. The static structure factor $S(k)$ of liquid krypton has been measured by neutron diffraction at temperatures $T = 130$, 169 and 199 K and at several densities. The extended k range of the measurements, 3.6–160 nm^{-1}, and the high accuracy of the data allow an unambiguous computation of the radial distribution function $g(r)$ and of the direct correlation function $c(r)$. All three functions, $S(k)$, $g(r)$ and $c(r)$, are in remarkably good agreement with the theoretical result when the Aziz pair interaction plus the triple-dipole three-body interaction are used in a triplet MHNC equation. We obtain definite evidence that the Lennard-Jones pair potential is not a good representation of the interatomic forces. The small remaining deviation between theory and experiment indicates the presence of some additional many-body force which is repulsive at short distance and attractive at intermediate distance.

1. Introduction

Rare gases are systems simple enough in their electronic structure that it is commonly believed that it should be possible to describe their thermodynamic and correlation properties on the basis of some simple interatomic interaction law. It is well established [1] that a pair-additive interaction is not adequate because the pair interaction $u_2(r)$ as determined by properties of the low-density gas and from atom–atom scattering data does not give a correct description of thermodynamic properties at higher density. The minimum additional term is a three-body interaction $u_3(r_1, r_2, r_3)$ which is usually taken to be of the Axilrod–Teller–Muto (ATM) form [2]. With this model of interaction the thermodynamics is well reproduced [3] but a potentially much more sensitive test is a comparison of the pair correlation function $g(r)$ or of the related static structure factor $S(k)$. On the other hand if at low density $S(k)$ is a faithful representation of $u_2(r)$, it is well known [4] that at high density the overall behaviour of $S(k)$ is dominated by excluded volume effects. There is not yet a clear cut answer to whether the measured $S(k)$ can reach the accuracy needed to probe the detailed shape of the interatomic interaction and whether the present models of the interaction are satisfactory. For instance the extensive measurement [5] of $S(k)$ in Kr along the room temperature isotherm gave evidence [6] of growing deviations from the theoretical $S(k)$ as the density increases. However, definite conclusions could not be drawn because the limited k range over which $S(k)$ was measured did not allow $g(r)$ to be deduced and because $S(k)$ at small k did not extrapolate well to the thermodynamic value of $S(0)$.

With this in mind we have undertaken a new study, experimental and theoretical, of the structure of Kr in the liquid phase at several densities and temperatures. Improvements

in neutron sources, diffractometers and analysis of the data allow $S(k)$ to be obtained with higher precision than before and over an extended k range. We stress that a real test of models of interatomic interactions can only be carried out if $S(k)$ is known over a large enough k range so that a meaningful $g(r)$ can be deduced via a Fourier inversion. If this is not the case quite different forms of interaction can reproduce the data to within a given uncertainty [7]. On the theoretical side we also have now integral equations [8] of high accuracy for $g(r)$ when a three-body interaction is present, so that a stringent test of interaction models can be performed.

The contents of the paper are as follows. Section 2 gives some theoretical background and the equations we are using. The experiment and analysis of the data are discussed in section 3 and in section 4 experiment and theory are compared in terms of $S(k)$, $g(r)$ and of the Ornstein–Zernike (OZ) direct correlation function $c(r)$. Section 5 contains our conclusions.

2. Theory and models of interaction

The function $g(r)$ completely characterizes the static correlations in a fluid at the pair level. It is related to the measured structure factor $S(k)$ by the relation

$$S(k) = 1 + n \int d^3r \, e^{ik \cdot r} [g(r) - 1] \tag{1}$$

where n is the number density. $g(r)$ is proportional to the probability of finding a couple of atoms at a distance r apart and it is normalized so that $g(r) = 1$ for uncorrelated particles. Therefore the quantity $H(k)$ defined by

$$S(k) = 1 + nH(k) \tag{2}$$

directly reflects the correlations in the fluid because it is simply the Fourier transform of $h(r) = g(r) - 1$. An equivalent representation of the pair correlations is via the direct correlation function $c(r)$, which is defined in terms of the OZ relation

$$g(r) - 1 = c(r) + n \int d^3r' \, c(r')[g(|r - r'|) - 1]. \tag{3}$$

In k space this becomes an algebraic relation so that $c(k)$ can be expressed in terms of $S(k)$ by

$$c(k) = [1 - S^{-1}(k)]/n. \tag{4}$$

$c(r)$ has an important theoretical role [4] and, in addition, it is a useful representation of the correlations because it reflects the interatomic interaction at intermediate and large distances more directly than $g(r)$.

In a classical system, as we assume here, $g(r)$ is a functional just of the interatomic interaction $U(r_1, \ldots, r_N)$ which we write in the form

$$U(r_1, \ldots, r_N) = \sum_{i<j} u_2(r_{ij}) + \sum_{i<j<l} u_3(r_i, r_j, r_l) \tag{5}$$

where r_i is the position of the ith atom, $r_{ij} = |r_j - r_i|$ and we have neglected many-body forces beyond the triplet level. A fundamental relation [4, 8] between correlations and interaction is given by

$$g(r) = \exp[-\beta u_2(r) + g(r) - 1 - c(r) + \mathcal{C}(r) + E(r)] \tag{6}$$

where $\beta = 1/k_B T$, $\mathcal{C}(r)$ is the dressed three-particles vertex

$$\mathcal{C}(r_{12}) = n \int d^3 r_3 \, g(r_{13}) g(r_{23}) \{\exp[-\beta u_3(r_1, r_2, r_3)] - 1\} \tag{7}$$

and $E(r)$ is the so called bridge function. This function is known only formally and in a diagrammatic language it is the sum of the infinite set of elementary diagrams. A useful approximation [9] consists in replacing $E(r)$ by the bridge function $E_{HS}(r; d)$ of hard spheres at the same density of the fluid and of a suitable diameter d. A variational principle [10] stipulates that the best choice of d is the value for which

$$\int d^3 r \, [g(r) - g_{HS}(r; d)] \frac{\partial E_{HS}(r; d)}{\partial d} = 0. \tag{8}$$

g_{HS} is the pair correlation function of the hard sphere system and E_{HS} can be obtained from equation (6) (in this case $\mathcal{C}(r) = 0$ and u_2 is the hard sphere potential) because an accurate parametrization of g_{HS} is known [11]. This produces the so-called triplet-MHNC equation [8], i.e. the MHNC equation extended to three-body forces. Thus our equation reads

$$g(r) = \exp[-\beta u_2(r) + g(r) - 1 - c(r) + \mathcal{C}(r) + E_{HS}(r)] \tag{9}$$

which together with (3), (7) and (8) forms a closed equation for $g(r)$ and this is solved by a suitable iterative method. If only two-body forces are present one has simply to drop the term $\mathcal{C}(r)$ in (9).

In a previous study [6] of Kr on the room temperature isotherm we have used a different version of MHNC, a crossover formulation [12]. That equation is more complex to use because the approximate bridge function contains three parameters so that in place of the single equation (8) one has a set of three additional equations which determines these parameters. The improvement given by the crossover MHNC is only marginal for the thermodynamic states of our experiment so in the present study we have used this triplet MHNC.

We have used for $u_2(r)$ the empirical pair potential HFD-B derived by Aziz and Slaman [13]. The Barker *et al* [14] pair potential gives a very similar pair-correlation function and we have also performed a few computations with the Barker pair potential as a check. For the three-body potential we have used the triple-dipole ATM form

$$u_3(r_1, r_2, r_3) = v(1 + 3\cos\phi_1 \cos\phi_2 \cos\phi_3)/r_{12}^3 r_{23}^3 r_{13}^3 \tag{10}$$

where ϕ_i are the angles of the triangle formed by r_i, $i = 1, 2, 3$, and $v = 220.4 \times 10^{-84}$ erg cm^9 [15]. For the relevant interatomic distances the quantity βu_3 is small so that in the expression of $\mathcal{C}(r)$ the exponential function can be expanded and truncated to linear order in u_3.

The Lennard-Jones (LJ) potential is believed to represent an 'effective' pair potential which gives a reasonably accurate representation of the rare gases in the medium-density regime. We have computed $g(r)$ and $S(k)$ with MHNC for the LJ potential

$$u_{LJ}(r) = 4\epsilon_{LJ}[(\sigma_{LJ}/r)^{12} - (\sigma_{LJ}/r)^6] \tag{11}$$

in order to test whether the accuracy of the measured $S(k)$ is such that it is possible to discriminate between different models of the interaction. Different values for ϵ_{LJ} and σ_{LJ} have been suggested for Kr and they fall in the range 160–180 K for ϵ_{LJ}/k_B and 0.36–0.37 nm for σ_{LJ}. We have used the values $\epsilon_{LJ}/k_B = 166.2$ K and $\sigma_{LJ} = 0.368$ nm [4] which give the best representation of the second virial coefficient. We have also performed some computations with different choices of ϵ_{LJ} and σ_{LJ} but, as will be discussed in the next section, this does not alter our conclusions.

Finally the measured $S(k)$ will also be compared with the structure factor $S_{HS}(k; d)$ of hard spheres (HS). S_{HS} is computed with the Verlet–Weis parametrization [11] and the diameter d is determined by the condition that the main peak of S_{HS} has the same height as the experimental $S(k)$.

3. Experiments and data analysis

The neutron diffraction measurements on Kr were performed at the Institut Laue–Langevin in Grenoble using the D4B diffractometer. The wavelength of the monochromatic neutron beam was $\lambda = 0.07054 \pm 0.00001$ nm and was determined by means of nickel powder diffraction. This wavelength allowed us to reach a maximum value of exchanged wavevector k of ~ 160 nm^{-1} with a resolution of $\Delta k/k \simeq 2\%$. The scattered intensities were measured with two ^{3}He multidetectors of which the first was placed at 1455 mm from the sample while the other was placed at 727 mm, allowing us to measure the two sets of k values $3.57 < k < 95.7$ nm^{-1} and $70.32 < k < 162.36$ nm^{-1} respectively. The data in the overlapping parts of the two ranges were used to connect the two sets of measurements. The efficiency of each multidetector cell was measured to an accuracy better than 0.1%. The measurements at each thermodynamic state were taken in repeated runs to judge the stability of the experimental set up. During the experiments the krypton samples were kept in a circular cylindrical vanadium container (height 63 mm, diameter 20.5 mm, wall thickness 0.5 mm) which was maintained at the desired temperature by means of an Orange ILL cryostat. The pure normal isotopic Kr mixture (99.995%) was introduced, during the experiment, into the scattering cell by means of a capillary line where pressure was measured with a calibrated pressure transducer.

In order to perform the background correction, including the correction for the neutrons scattered from the container and the tail of the cryostat, we used the ^{3}He technique [16] which consists in measuring the neutrons scattered by the system after having replaced the Kr sample with an amount of ^{3}He such that the macroscopic total cross section of the Kr sample and the corresponding absorption cross section of ^{3}He are equal. This technique is useful because it considerably simplifies the data correction with respect to the technique [17] in which the empty beam and empty container scattered intensities are measured. The measuring time was chosen at each measured density in such a way that a statistical precision of $\sim 0.1\%$ on the counting could be achieved. The Kr scattering data were then corrected for background, multiple scattering (including scattering between the sample and the container and the Va tail of the cryostat), attenuation effects and inelastic scattering. We also applied a correction in order to replace the nominal scattering angle by the average scattering angle, this difference being due to the finite size of both the sample and the detector cells.

When the measured intensities are available in a sufficiently large k range the absolute normalization of $I(k)$, which is necessary to derive the structure factor $S(k)$ from the measured intensities corrected as previously discussed, can be performed by using the fact

that $S(k)$ converges to unity for high k values [16]. The structure factor is then derived by means of the knowledge of σ_S and σ_c which are the total and the coherent scattering cross sections, respectively. In the case of Kr the published values of the ratio σ_S/σ_c are spread out over a range of about 10% [5, 18], even though the latest published compilation [19] gives an estimate of 2.2% for the error on the recommended value.

Since we aimed at a better final accuracy for the $S(k)$ values, we have adopted for the normalization and the subsequent derivation of the structure factor a procedure [20] based on the facts that (a) $S(k)$ at high k values converges to unity and (b) $S(k = 0)$ is given by the compressibility theorem according to

$$S(0) = nk_B T \chi_T \qquad (12)$$

where χ_T is the isothermal compressibility. The values of χ_T for our experimental states have been derived from the thermodynamic data of [21]. This procedure can be applied because of the high precision of our data and the well optimized k range of our measurements. The value of the ratio σ_S/σ_c is thus determined by the normalization itself [20]. The extrapolation of the experimental data toward $k = 0$ has been performed following the theoretical behaviour calculated by means of the two- and three-body potentials as explained in the previous section. We have also verified that the extrapolation is model independent within the required precision [20]. The normalization has been performed for the measurement of $S(k)$ at $T = 169$ K and $n = 14.57$ nm^{-1} because in this case the theoretical calculation converges almost exactly to the thermodynamic limit. In addition the density is not too large and this is the region where the MHNC equation is known [7] to be very accurate. The value of σ_S/σ_c obtained by means of this procedure is $\sigma_S/\sigma_c = 1.068 \pm 0.002$. This value has been then used in order to derive $S(k)$ for all the other measured thermodynamic points. It is worth noticing that this value for σ_S/σ_c, which is different from the value $\sigma_S/\sigma_c = 1.001 \pm 0.022$ of the latest compilation found in the literature [19], does not represent the result of a direct measurement of the ratio of the cross sections; in our case it could also contain small contributions from systematic errors in the calculations of the corrections to the measured intensities. A detailed analysis [20] shows that these errors should be essentially k independent so that our procedure removes their effects. The accuracy of our normalization procedure is determined by the accuracy of the data of our experiment, of the compressibility χ_T and of the extrapolation toward $k = 0$; we estimate that the absolute error introduced in $S(k)$ by this procedure is of the order of 0.002.

The measurements were performed at seven different thermodynamic states in dense fluid Kr below the critical temperature; table 1 reports temperatures and densities of the seven states. The accuracy of the temperature determination was 0.1 K, while the pressure was determined with an accuracy of 0.01 bar. The densities were derived by means of the p, V, T measurements of Street and Staveley [21] and they are given with an accuracy better than 0.01 nm^{-3}.

From our measured $S(k)$ we also derived, by means of equation (2), $H(k)$ which more directly reflects the interparticle correlations. Our data have a very smooth variation with k over all the measured range as can be seen in figure 1 for the measurement at $T = 199$ K and $n = 11.86$ nm^{-3}. This is very close to one of the states ($T = 200$ K, $n = 11.55$ nm^{-3}) of the measurements of Fredrikze [22] and these data are also shown in figure 1. There is an overall agreement but well defined deviations are also present. This is most noticeable in the small-k region, but also the height of the main maximum is somewhat different. It is clear that we have more regular data both at small and at large k. We also notice that the

Table 1. Temperature and density of the measured states.

	T (K)	n (nm^{-3})
1	169.07	14.57
2	169.22	14.40
3	169.08	14.25
4	199.22	11.86
5	199.09	11.28
6	130.06	17.01
7	130.06	16.83

low-k part of $H(k)$ shows that our data in this region behave more consistently with the $S(0)$ value derived from the isothermal compressibility data. This consistency is also true for the other thermodynamic states as it will be shown in detail in the next section.
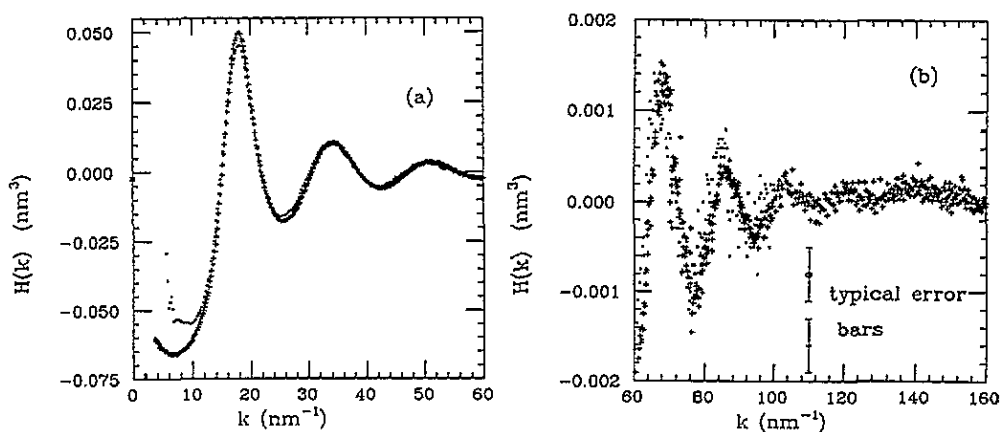
Figure 1. $H(k)$ of Kr from our measurement 4 ($T = 199$ K and $n = 11.86$ nm^{-3}) (+), from Fredrikze [22] ($T = 200$ K, $n = 11.55$ nm^{-3}) (●) and from the compressibility data at $k = 0$ (∗). In (a) the error bars of the present measurement are below the size of the symbols.

The states of our seven measurements are grouped at closely separated densities at three different temperatures, 199 K, 169 K and 130 K. Here we discuss only one measurement at each temperature, i.e. experiments 1, 4 and 7. The small variation of the measured $S(k)$ at the neighbouring states will be discussed separately because it will give access to the density derivative of $S(k)$.

The overall behaviour of $S(k)$ for these three states is shown in figure 2. On such a scale the data are almost indistinguishable from the theoretical result for the Aziz pair interaction plus the ATM three-body one. The motivation for having performed the measurements over an extended k range is to compute in a reliable way $h(r) = g(r) - 1$ from

$$h(r) = \frac{1}{2\pi^2 r} \int k H(k) \sin(kr) \, dk. \tag{13}$$

Different rules have been used in the past to extend $H(k)$ outside the measured range. Here we have used a simple method which depends on the fact that the theoretical $H(k)$ is in

very good agreement with the data. In the range $60 < k < 100$ nm^{-1} theory and experiment agree to within the experimental error so that in computing $h(r)$ we use the theoretical $H(k)$ in the range 100–300 nm^{-1} and beyond this range we put $H(k) = 0$. For $k < 3.7$ nm^{-1} the $H(k)$ of experiments 1 and 7 is joined with the compressibility value $H(0)$ again by the theoretical $H(k)$ displaced by the small amount necessary to join it smoothly with the experimental thermodynamic limit. For experiment 4 the extrapolation in the same region is made with a fourth-order in k polynomial.
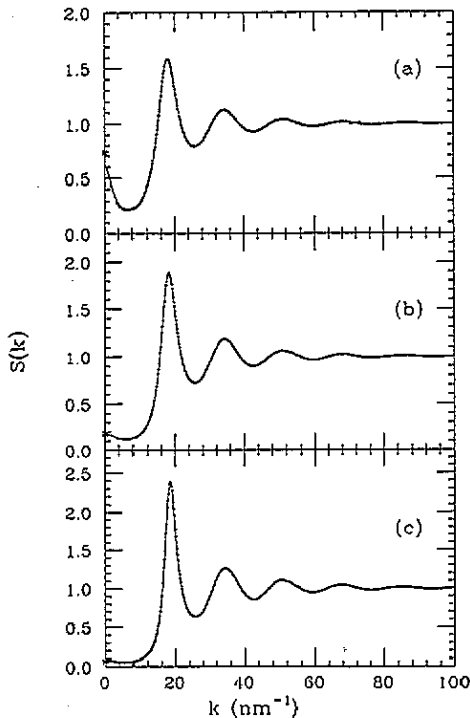

Figure 2. $S(k)$ over the $k < 100$ nm^{-1} range of measurement at (a) $T = 199$ K, $n = 11.86$ nm^{-3}, (b) $T = 169$ K, $n = 14.57$ nm^{-3}, (c) $T = 130$ K, $n = 16.83$ nm^{-3}. The full curve is the result of the triplet MHNC equation with the Aziz pair interaction plus the three-body ATM term. Value at $k = 0$ from the compressibility data (∗).
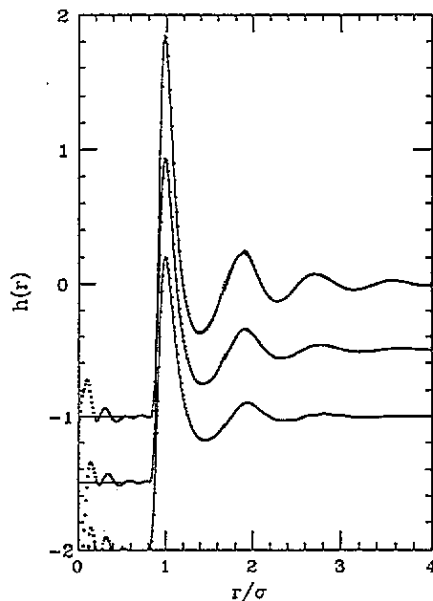
Figure 3. Theoretical (full curve) and experimental (points) $h(r)$: from top to bottom we display $h(r)$ corresponding to (c) of figure 2, $h(r) - 0.5$ corresponding to (b) and $h(r) - 1$ corresponding to (a). $h(r)$ is plotted as a function of r/σ where $\sigma = 0.4008$ nm is the position of the minimum of the Aziz pair interaction.

In figure 3 we show the resulting three $h(r)$ together with the theoretical result. It is clear that there is an impressive agreement between theory and experiment. A very stringent test on the accuracy of the measured $S(k)$ and of the extension of the data is given by the condition that $g(r) = 0$ (i.e. $h(r) = -1$) at short distance corresponding to the essentially impenetrable core. Different sources of error and the approximation inherent to the extension of the data at small and large k prevent the exact fulfilment of this condition but the small amplitude of the oscillations around -1 and their symmetrical shape indicate the accuracy of the data and that the extension method is accurate enough.
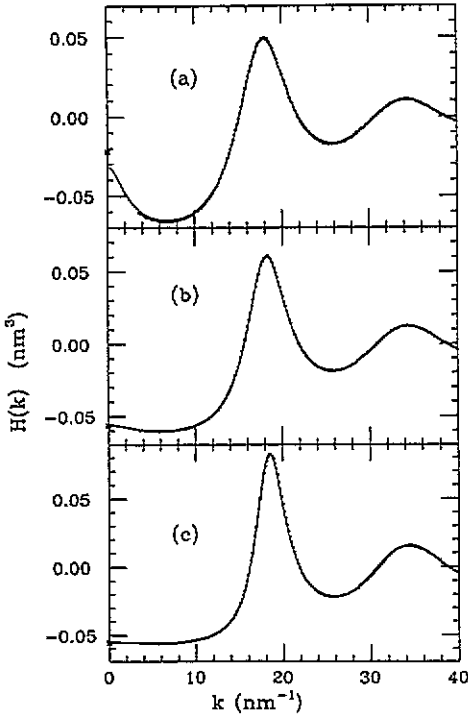
Figure 4. Detail of $H(k)$ in the small–intermediate-k range. (a), (b) and (c) as in figure 2.
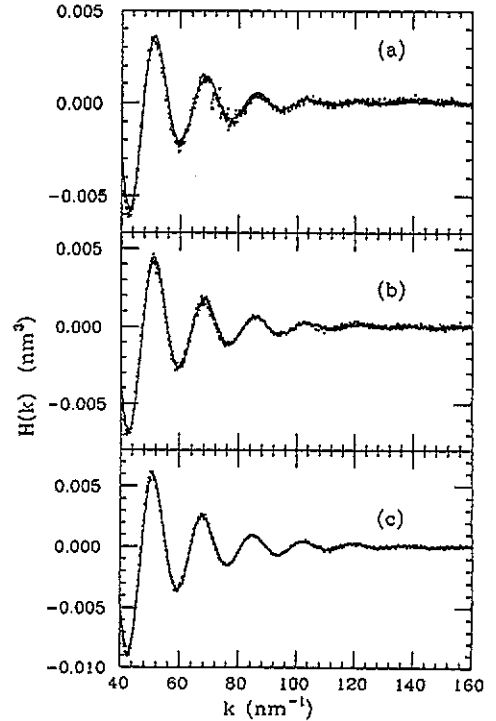
Figure 5. Detail of $H(k)$ in the large-k range. (a), (b) and (c) as in figure 2.

4. Structural data and models of interaction

We show in figures 4 and 5 respectively the low- and high-k behaviour of $H(k)$ for the three states we have considered in the previous section. We show also the computed $H(k)$ with the triplet MHNC equation as discussed in section 2. The Aziz pair interaction plus the ATM three-body term is used. From the comparison between the experimental and calculated $H(k)$ we can deduce the following: firstly there is a striking agreement at the lower density, i.e. the higher temperature, while increasing the density and lowering the temperature the agreement is still very good but some deviations are apparent in the region of the first two peaks and valleys; secondly at the higher density the experimental $H(k)$ has a convergence to the thermodynamic value of $H(0)$ as good as the theory. Notice that at $k = 0$ the quantity most significant is $S(0)$ which has a direct physical meaning. At $T = 130$ K and 169 K theory reproduces the compressibility value of $S(0)$ to within 8% and 4% respectively, and the theoretical value is larger than experiment. At the lower temperature $T = 130$ K our experimental $S(k)$ at small k is quite consistent with the value of $S(0)$. At $T = 169$ K the comparison is not significant because these data have been used to fix the value of σ_S/σ_c. At the higher temperature $T = 199$ K there is a significant OZ behaviour at small k, signalling that the critical point ($T_c = 209$ K and $n_c = 6.5$ nm^{-3}) is not very far. In this situation the measurement does not extend to small enough k to allow a reasonable extrapolation to $k = 0$. On the other hand theory gives a significantly lower value of $S(0)$, by 20% with respect to the compressibility value. We have verified that the crossover MHNC does not give a significantly different value of $S(0)$. In the region of the critical point and around

it there is a very delicate balance between attractive and repulsive forces and the deviation in $S(0)$ at $T = 199$ K between theory and experiment is probably due to some additional interatomic force.

We consider now how different models of interaction affect the correlations and how these compare with experiment. We start with the comparison in r space and in order to demonstrate the deviations we show in figure 6 the difference

$$\Delta h(r) = h_{\text{exp}}(r) - h_{\text{MHNC}}(r) \qquad (14)$$

between the $h(r)$ deduced from the experimental $S(k)$ as discussed in the previous section and the MHNC result for different model interactions. We display the result for the Aziz interaction plus the ATM three-body term, for the Aziz-only interaction and for the LJ interaction. The Aziz plus three-body interaction is consistently the best for all three thermodynamic states with $|\Delta h|$ below 0.07 at all r. The three-body interaction does not have a large effect on $h(r)$ but it is clearly visible that the presence of three-body forces improves the description of $h(r)$, in particular at short distance up to the first maximum of $h(r)$. $\Delta h(r)$ for the LJ interaction is much larger for all three states. The effect is most striking at short distance where $|\Delta h|$ is more than five times larger than for the best model interaction but at larger distance also the LJ model is clearly inferior.

In a similar way we present in figure 7 the deviations

$$\Delta S(k) = S_{\text{exp}}(k) - S_{\text{MHNC}}(k) \qquad (15)$$

for the three models of interaction we have considered, the Aziz pair interaction with and without the three-body interaction and the LJ interaction. Here we also consider the deviation from the $S_{\text{HS}}(k)$ of hard spheres. Here again the result for the Aziz plus three-body interaction is by far the best, at the two higher temperatures $|\Delta S|$ is below 0.02 at all k. At $T = 130$ K ΔS becomes of the order of 0.05 but in this case this deviation is at least in part due to the inaccuracy of the MHNC equation as we discuss below. Only at $T = 199$ K does the three-body interaction give a sizeable contribution to $S(k)$ and better agreement with experiment is obtained when the three-body interaction is present. At the two lower temperatures and higher densities the effect of u_3 is appreciable only in the neighbourhood of $k = 0$. With the LJ potential $\Delta S(k)$ is typically five to ten times larger than for the best interatomic model and only the thermodynamic value $S(0)$ is rather accurate (see table 2). $\Delta S(k)$ for the LJ potential is particularly large at the main maximum of $S(k)$ and this corresponds to a shift and to a different height of this peak compared to experiment (see table 2). The degree of discrepancy between experiment and the LJ result depends on the values which are used for ϵ_{LJ} and σ_{LJ}. Other choices of ϵ_{LJ} and σ_{LJ} in the range indicated in section 2 do not modify in a significant way the deviations from experiment, so the results presented in the figures are typical of the LJ potential.

As it is expected theoretically, $S_{\text{HS}}(k)$ gives a rather good description of $S(k)$ at the higher density and up to the first maximum of $S(k)$. In this region it is much better than the LJ interaction and not much worse than the Aziz one. At larger k, of course, $S_{\text{HS}}(k)$ has large deviation from experiment. As we move to lower density the deviation ΔS for the HS model becomes significant over all the k range.

From the previous comparisons we can conclude that the LJ potential is clearly inadequate to represent the correlations in Kr for all the thermodynamic states we have investigated. When the Aziz form is used for the pair potential there is a clear indication that the three-body ATM interaction brings theory in better agreement with experiment both
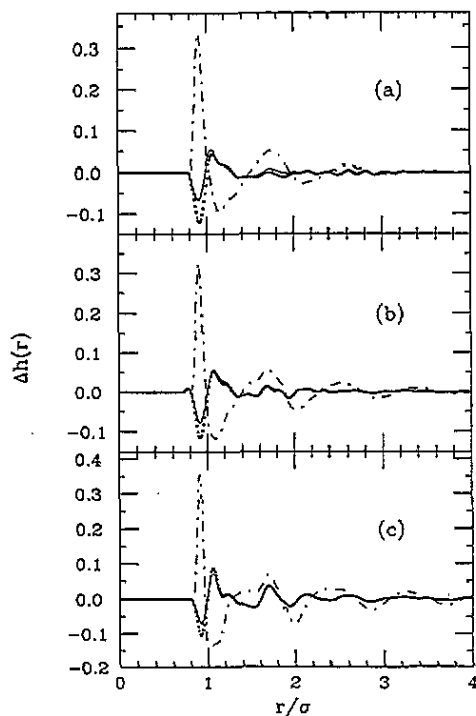
Figure 6. Difference $\Delta h(r) = h_{exp}(r) - h_{MHNC}(r)$ for the Aziz pair interaction with (full curve) and without (points) the ATM three-body interaction and for the LJ interaction (chain curve). Thermodynamic states are as in figure 2 and reduced r units as in figure 3.
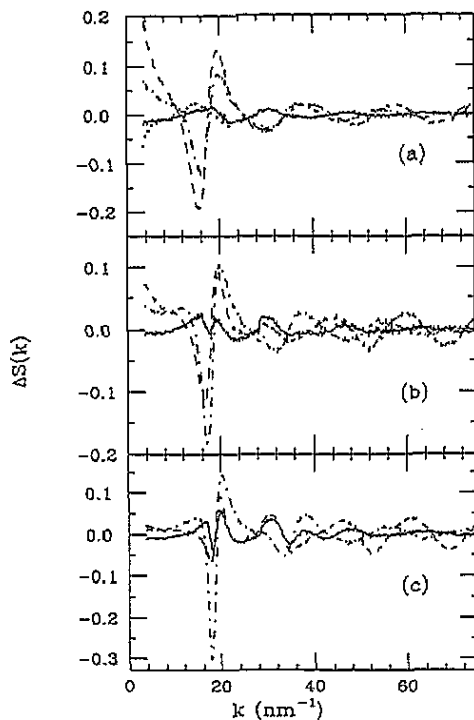
Figure 7. Difference $\Delta S(k) = S_{exp}(k) - S_{MHNC}(k)$ for the Aziz pair interaction with the ATM three-body term (full curve), for the LJ interaction (chain curve) and for hard spheres (broken curve). The result for the Aziz interaction without the three-body term (points) is only shown in (a) up to 20 nm^{-1}. In the other cases the result is almost coincident with the full curve. Thermodynamic states are as in figure 2.

in r and in k space. Correlations, not shown here, computed with the Barker *et al* [14] pair interaction are very close to the results with the Aziz one and we cannot discriminate between these two models of pair interaction on the basis of our measurements.

We consider now the significance of the remaining deviations between experiment and the results for the best model potential, i.e. the Aziz pair potential plus three-body ATM term. For all three thermodynamic states the main deviation in Δh is present at small r (cf figure 6) with a negative dip followed by a positive maximum, and this corresponds to a small inward displacement of the main maximum of the theoretical $h(r)$ and also to a slightly higher peak (see table 2). This indicates that the interatomic forces should be slightly more repulsive at short distance. At larger distance $\Delta h(r)$ is below the noise level in the case of $T = 199$ K whereas at the lower temperature $T = 130$ K, corresponding to the larger density, some deviation persists at larger r. If the bridge function of MHNC were exact we could infer from $\Delta h(r)$ what is the missing interaction. This $\Delta u_{eff}(r)$ is the quantity which has to be added to the Aziz $u_2(r)$ in order that equation (9) is satisfied when $g(r)$ is the experimental value and $c(r)$ is the corresponding OZ direct correlation as obtained by the inverse Fourier transform of equation (4). Thus $\Delta u_{eff}(r)$ is given by

Table 2. $S(0)$, position and value of $S(k)$ (k_M and S_M) and $g(r)$ (r_M and g_M) at the main maximum. Experimental value (exp) and MHNC results are given for the Aziz pair interaction plus ATM three-body term (Az+3b), for the Aziz pair interaction (Az) and for the Lennard-Jones interaction (LJ).

	$S(0)$	k_M (nm^{-1})	S_M	r_M (nm)	g_M
$T = 199.22$ K; $n = 11.86$ nm^{-3}					
exp	0.736	18.01	1.59	0.3974	2.20
Az+3b	0.625	17.91	1.57	0.3952	2.20
Az	1.256	17.97	1.58	0.3945	2.24
LJ	0.413	17.46	1.61	0.4025	2.13
$T = 169.07$ K; $n = 14.57$ nm^{-3}					
exp	0.177	18.27	1.89	0.3955	2.42
Az+3b	0.184	18.16	1.88	0.3941	2.45
Az	0.265	18.20	1.88	0.3936	2.47
LJ	0.121	17.84	1.99	0.3995	2.46
$T = 130.06$ K; $n = 16.83$ nm^{-3}					
exp	0.066	18.55	2.38	0.3945	2.84
Az+3b	0.071	18.49	2.40	0.3935	2.86
Az	0.092	18.49	2.38	0.3931	2.87
LJ	0.048	18.29	2.60	0.3974	2.95

$$\Delta u_{\text{eff}}(r) = k_B T [g_{\exp}(r) - 1 - c_{\exp}(r) - \ln g_{\exp}(r) + \mathcal{C}(r) + E_{\text{HS}}(r; d)] - u_2(r). \tag{16}$$

In figure 8 this excess effective pair interaction is shown for the three states. Notice that this Δu_{eff} does not have to be a pair interaction, but can be the effective two-body contribution due to three-body forces in excess of the ATM term or to four or higher-order terms. The common feature of Δu_{eff} is the presence of additional attraction at medium distance and of repulsion at shorter distance. For comparison we show also $-k_B T \mathcal{C}(r)$, i.e. the effective two-body contribution due to the ATM three-body interaction, and the Aziz $u_2(r)$.

Clearly the reliability of the computed Δu_{eff} depends critically on the accuracy of the MHNC equation, i.e. on the modeling of the bridge function. In case of the higher-density state we have a way to probe this by using $g(r)$ from an accurate simulation [7] for the LJ potential. With the parameter for Kr the simulation corresponds to $T = 124.65$ K and $n = 16.86$ nm^{-3}, which is very close to our experiment 7. In figure 9 we compare $\Delta h(r) = h_{\text{SIM}}^{(\text{LJ})}(r) - h_{\text{MHNC}}^{(\text{LJ})}(r)$ for the LJ interaction to $\Delta h(r) = h_{\exp}(r) - h_{\text{MHNC}}(r)$ for the Aziz plus ATM three-body term. It is clear that for $r/\sigma \gtrsim 1.5$ ($\sigma = 0.4008$ nm) the two Δh are very similar and we can infer that here the deviation between theory and experiment is mainly due to the approximation of MHNC. On the other hand for $r/\sigma < 1.5$ the two $\Delta h(r)$ are rather different, so the deviation from experiment must be genuine. It is possible to estimate approximately how the MHNC approximation on the bridge function affects $\Delta u_{\text{eff}}(r)$. In fact it is known [9] that the bridge function is not very sensitive to the details of the interatomic interaction, so we can assume that the difference ΔE_{Kr} between the exact (but unknown) bridge function of Kr and the MHNC approximation is equal to the difference

$$\Delta E_{\text{LJ}}(r) = E_{\text{exact}}^{\text{LJ}}(r) - E_{\text{MHNC}}^{\text{LJ}} \tag{17}$$

between the exact and the MHNC approximation in the case of the LJ interaction. $E_{\text{exact}}^{\text{LJ}}$ has been deduced [7] from simulation results, so ΔE_{LJ} is known. Therefore an improved
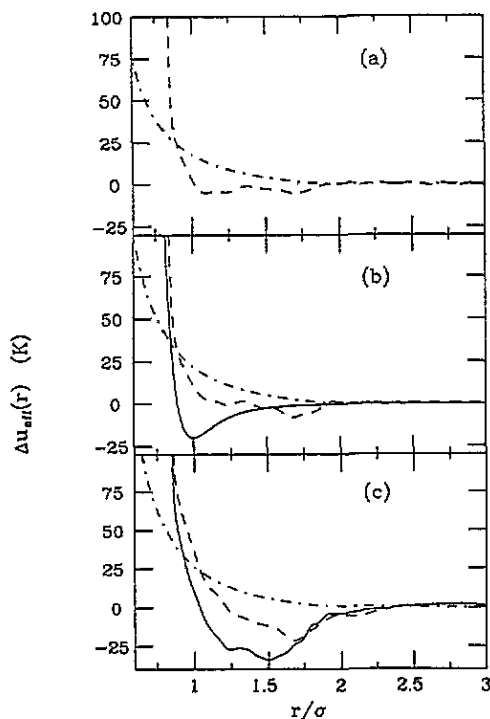
Figure 8. Excess effective pair interaction as given in (16) (broken curve) for the thermodynamic states as in figure 2. The chain curve represents $-k_B T C(r)$ (7), i.e. the effective pair interaction corresponding to the three-body ATM interaction. In (b) the full curve represents the Aziz $u_2/10$ and in (c) the full curve represents $\Delta u_{\text{eff}}(r)$ when the correction (17) to the bridge function is included. Reduced r units are as in figure 3.

estimate of the excess interaction $\Delta u_{\text{eff}}(r)$ is obtained from equation (16) when E_{HS} is replaced by $E_{\text{HS}}(r; d) + \Delta E_{\text{LJ}}(r)$. This Δu_{eff} is also shown in figure 8(c). A large part of the excess repulsion given by (16) in the range 0.4–0.6 nm is seen to be an artifact of the MHNC equation, but also the improved estimate of Δu_{eff} gives an indication of a slightly stronger repulsion at short distance and more attraction in the range 0.6–0.8 nm. This qualitative feature is similar to that of $\Delta u_{\text{eff}}(r)$ for the other two states, and this adds strength to the conclusion that this is a genuine feature. The fact that the amplitude of Δu_{eff} changes with density and temperature indicates that Δu_{eff} should arise from many-body forces. However, the details of Δu_{eff} cannot be taken too seriously because MHNC is not accurate enough for this purpose. A more elaborate theoretical scheme, like the iterative predictor–corrector method [7], should be used. Also, a more elaborate scheme of extension of the experimental $S(k)$ at small and large k should be used in order to reduce the short-scale oscillations of $g(r)$.

The final comparison concerns the OZ direct correlation function $c(r)$. The experimental $c(r)$ is deduced from (4) and in figure 10 this is compared to the MHNC result for the Aziz plus the ATM three-body term. For $c(r)$ also there is a very good agreement between theory and experiment. In figure 11 we show the difference $\Delta c(r)$ between experiment and theory for the LJ potential also. There is again a large improvement when the more accurate representation of the interatomic forces is used.
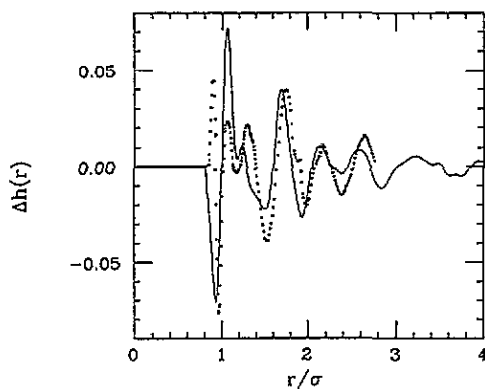
Figure 9. The full curve represents $\Delta h(r) = h_{exp}(r) - h_{MHNC}(r)$ as in figure 6(c) and points represent $\Delta h(r) = h_{SIM}(r) - h_{MHNC}(r)$ for the LJ potential. Reduced r units as in figure 3.
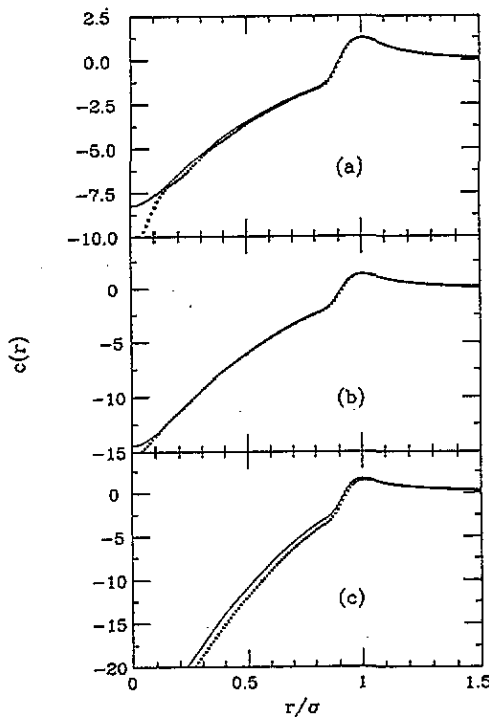

Figure 10. Direct correlation function: experiment (points) and theory (full curve) as in figure 2.

5. Conclusions

The main conclusion of our work is that it is possible to obtain structural information on a simple liquid with the precision needed to obtain reliable information on the interatomic forces. We believe that for the first time we have shown that in the liquid phase also the LJ potential does not give a realistic representation of the interatomic forces in a rare gas such
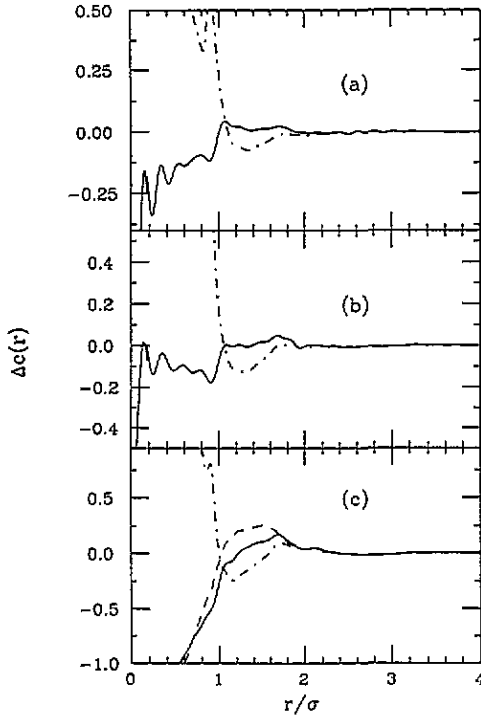
Figure 11. Difference $\Delta c(r) = c_{exp}(r) - c_{MHNC}(r)$ for the Aziz pair interaction plus the three-body ATM term (full curve) and for the LJ interaction (chain curve). In (c) $\Delta c(r)$ is also shown for the Aziz plus ATM term when the improved MHNC is used that includes the correction (17) to the bridge function (broken curve). Thermodynamic states are as in figure 2.

as Kr. On the other hand, the Aziz pair interaction gives an excellent representation of the structure of Kr for all the thermodynamic states of our measurement. The difference between the Aziz and the Barker *et al* pair interaction, is too small and we cannot discriminate between them on the basis of our data. In addition, we find evidence that again at the level of structural data the presence of the triple-dipole three-body forces gives an improved description of the system. It is gratifying that thermodynamic and structural data give a concordant indication in favour of the ATM three-body forces.

At the level of pair correlations there is only one independent function. However, it is useful to compare theory and experiment in terms of all three functions, $S(k)$ or $H(k)$, $g(r)$ or $h(r)$ and $c(r)$, and this is for several reasons. The direct physical meaning of $g(r)$, for instance, can help us to understand the limitation of a model of the interatomic interaction and, at the same time, represents a very strong constraint on the accuracy of the experimental data for $S(k)$ via the condition that $g(r)$ vanishes at short distance. On the other hand the effect of a certain interaction term can be concentrated on one of these correlation functions and in a certain range. For instance the stronger evidence from structural data for the ATM three-body interaction comes from the behaviour of $g(r)$ at short distance. In this respect it is important to have an accurate theory of correlations which is also able to treat the presence of three-body forces, and this is the case with the triplet MHNC equation that we have used. This is because such a theory gives access to all these correlation functions and there is no size effect to worry about, as in simulation. However, we have evidence that for

the state of higher density close to the triple point, experiment shows the limit of accuracy of the MHNC equation. In fact, the small remaining difference between the experimental and the theoretical $h(r)$ has some features in common with the deviation between theory and the result of an accurate simulation for the LJ potential. By taking this into account we are able to estimate the excess effective pair interaction Δu_{eff} implied by the small remaining deviation between theory and experiment. For all the states of our experiment Δu_{eff} is repulsive at short distance and attractive at intermediate distance. The magnitude of Δu_{eff} is only a small fraction of the Aziz pair interaction and, at the two higher temperatures, also smaller than the effect of the three-body ATM term. Δu_{eff} becomes larger at the higher density, so the origin of this extra interaction should be in additional three-body or higher order forces. However, these effects on correlation functions are fairly small and a quantitative assessment of the excess interaction Δu_{eff} requires either an integral equation substantially more accurate than MHNC, which is not available to our knowledge, or a symbiotic use of the integral equation with simulation methods. At the same time the effect of the uncertainty in the experimental $S(k)$ and $h(r)$, arising, for instance, from the adopted value for σ_S/σ_c and from the method of extension of $S(k)$ at small and large k, should be carefully estimated.

If it is true that all $S(k)$ of liquids are very similar, we have shown that the information contained in $S(k)$ is very rich and the signature of the interatomic forces is contained in the data at the level of experimental precision which is presently available.

Acknowledgments

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