Many-body interaction effects on the low-k structure of liquid Kr

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Neutron diffraction measurements and theoretical calculations of the structure factor $S(k)$ of liquid Kr are extended to small k values ($k<4$ nm^{-1}). The results show that many-body interaction contributions have an increasing effect on $S(k)$ as $k\to 0$, reaching at least 40% of the measured intensity. Both the phase diagram and the low-k structural data of dense Kr turn out to be closely reproduced by the hierarchical reference theory if additional many-body forces are taken into account by an augmented strength of the Axilrod-Teller triple-dipole potential. The experimental density derivative of $S(k)$ is also used for a very sensitive test of the theories and interaction models considered here.

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Considerable progress in the understanding of three- and more-body potential effects in fluids has been made through the joint use of accurate neutron diffraction determinations of the static structure factor $S(k)$ and of theories developed to predict the structure of simple fluids over wide density, temperature, and exchanged momentum domains [1–9]. Most of these studies show that good agreement between theory and experiment is often found when the calculations use a realistic pair potential, along with the long-range triple-dipole contribution, i.e., the well-known Axilrod-Teller (AT) model [10].

In spite of the advances made in the field, a complete knowledge of many-body effects on $S(k)$ of dense fluids is, however, still lacking, even in the simplest case of rare-gas fluids. This has been evidenced by the results of a previous study on liquid Kr [3], based on the comparison between wide-angle ($k>3.5$ nm^{-1}) neutron diffraction data and modified hypernetted chain (MHNC) [11–13] calculations, using the well tested Aziz-Slaman (AS) pair potential for Kr [14], with and without AT forces. Here the MHNC outputs reveal that $S(k)$ is heavily influenced by the triplet AT interactions mainly for $k<3$ nm^{-1}. This suggests, as observed in Ref. [3], that more complete information on the size and the nature of structural many-body effects in liquids can be achieved by extending the diffraction measurements to that region.

On the other hand, it is worth mentioning that liquid state theories have been developed recently, like the soft-core hierarchical reference theory (SC-HRT) [5,15], which are suitable for the description of the dense fluid properties in a wide range of thermodynamic states, also near to liquid-vapor coexistence, and which can be used for comparison with experimental findings.

Here we report the results of a low-k neutron diffraction investigation in liquid Kr and the comparison with SC-HRT and MHNC calculations. The measurements, performed at Laboratoire Léon Brillouin (Saclay, France) with the small-angle diffractometer PAXE covering the range $0.8<k/\mathrm{nm}^{-1}<4.1$, match some of the thermodynamic states studied by wide-angle diffraction in Ref. [3]. Three states at $T=199$ K, with number densities $n=11.31$, 11.66, and 12.10 nm^{-3}, and two states at 169 K, namely, $n=14.23$ and 14.57 nm^{-3}, were thus considered, varying approximately from 1.7 to 2.2 times the Kr critical density ($n_c=6.55$ nm^{-3} and $T_c=209.39$ K). The measured intensities were corrected for background, multiple and incoherent scattering, attenuation, and inelasticity effects. Data calibration was accomplished by means of an additional measurement on dilute methane, which is a predominantly incoherent neutron scatterer. The statistical accuracy reached in our runs led to structure factor determinations with about 2.5% relative uncertainty, after the final absolute normalization of each $S(k)$ to the corresponding thermodynamic limit at $k=0$, calculated from the equation-of-state data of Jùza and Sifner [16] through $S(0)=nk_BT\chi_T$, where χ_T is the isothermal compressibility. It is worth stressing that the present $S(k)$ determination at low k, i.e., in the wave vector region which is heavily affected by many-body effects, fills most of the existing gap between the higher-k data of Ref. [3] and the $S(0)$ thermodynamic results, giving therefore the possibility of analyzing the k dependence of those contributions.

The thermodynamic states of the experiment are rather close to the liquid boundary of the liquid-vapor phase transition. It is important then to make a comparison with a theory which describes well this phase boundary. The hierarchical reference theory (HRT) is a suitable choice. This theory implements the renormalization group strategy within the liquid-state theory. One important feature is that the HRT equation is able to generate the liquid-vapor phase boundary. The general HRT strategy is applied within an Ornstein-

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Zernike approximation for a soft-core potential (SC-HRT) which has been used earlier above T_c [5]. Tests of the theory below T_c, performed by comparing HRT and simulation data for a Lennard-Jones fluid on the coexistence curve, provided remarkable results [15]. In particular, at the critical point, HRT was found to reproduce the simulation output for n_c almost exactly and for T_c within 1%.

Having an accurate theory for most thermodynamic fluid states, we can now use it to probe the interaction features in a dense rare gas, such as liquid Kr, by including a realistic model of the interatomic potential in the SC-HRT equation and by comparing the theoretical results with experimental quantities. First important indications are obtained through the analysis of the experimental phase diagram and, in particular, of the critical parameters [16]. We find that, by using the AS potential for the two-body interaction and the three-body AT potential with the standard value of its strength ν in Kr, $\nu = 2.204 \times 10^{-26}$ J nm^9 [17], SC-HRT provides a critical temperature and density which are, respectively, about 5% and 3% larger than the corresponding experimental values. Even higher values are obtained without three-body forces. The above deviations from experiment are much larger than the expected 1% accuracy of HRT. We have performed various tests to prove that the way in which we treat the three-body AT interaction is not responsible for the discrepancy in n_c and T_c. We take this as evidence that the main origin of the above deviation is due to an inadequate representation of the true interatomic potential.

It is known that the triplet potential contains terms in addition to the AT one, and also four-body and higher orders might contribute to the total interaction. In the absence of detailed information on such additional many-body contributions, we may try to assume that they can be represented by the AT potential with a renormalized intensity ν_{eff} (referred to in the following as AT$_{eff}$). We find that if we take $\nu_{eff} = 1.65\nu$, the position of the critical point is displaced at $T_c = 211.1$ K and $n_c = 6.54$ nm^{-3}; i.e., both T_c and n_c are within 1% from experiment. Such an agreement is now present also for the phase diagram below T_c. As an example, for the two isotherms of the present measurements of $S(k)$, we find $n_{vap} = 2.64$ nm^{-3} and $n_{liq} = 11.0$ nm^{-3} at $T = 199$ K (experimental values are 2.63 and 10.9 nm^{-3}, respectively) and $n_{vap} = 0.84$ nm^{-3} and $n_{liq} = 14.04$ nm^{-3} at $T = 169$ K (against 0.80 and 14.10 nm^{-3}, respectively, from experiment). This is the first time that one gets such a close agreement with the experimental phase diagram starting from a microscopic theory with a realistic model of the interatomic interaction.

The HRT equation produces not only the thermodynamic quantities, but also the pair correlation. It is then possible to test the overall agreement with experiment for $k > 0$ and, in particular, the accuracy of the above effective interaction, by comparison with our experimental results for $S(k)$ and its density derivatives.

Figure 1 shows the measured structure factors at 169 K and 199 K, together with the results of SC-HRT calculations based on the AS plus AT$_{eff}$ model. At 199 K, calculations without many-body forces are also shown for the 11.66 and 12.10 nm^{-3} states [Fig. 1(b)]. It is clear that a pure two-body interaction is unable to account for the experimental behavior for $k < 4$ nm^{-1}, with differences increasing to about 40% at the lowest experimental k value (0.8 nm^{-1}). Conversely, by adding the effective AT interaction, SC-HRT provides, for all the densities studied on the 199 K isotherm, a very good description of the experimental $S(k)$ down to $k \sim 1.2$ nm^{-1}. Below this k value, differences between data and calculations (slightly increasing as the coexistence curve is approached, i.e., as the density is decreased) are anyway reduced to 7% or less by the introduction of the effective three-body potential. A similar small deviation is found for both densities at 169 K, where the slight underestimation by SC-HRT of the experimental data is detectable, however, in a wider k range ($k < 3.5$ nm^{-1}) and appears to be systematic.

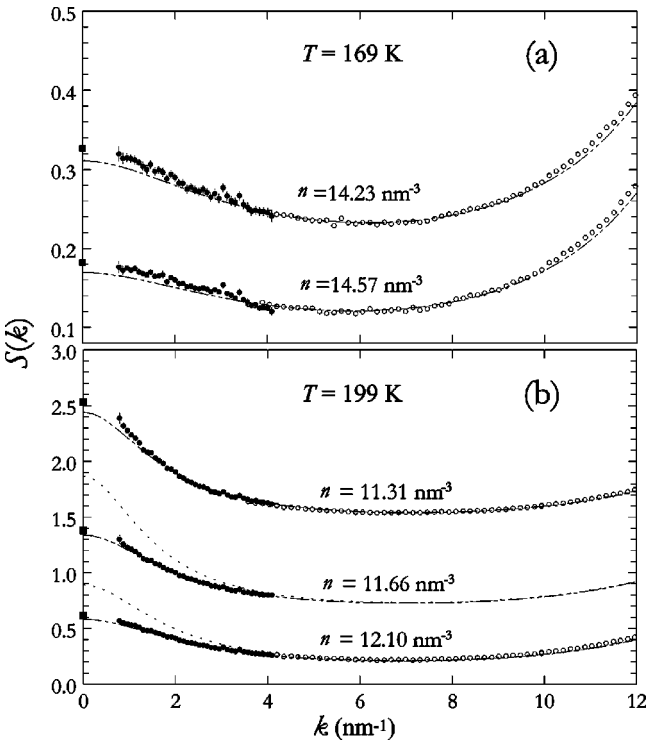

FIG. 1. Experimental low-k $S(k)$ (dots with error bars) compared with the results of SC-HRT calculations for the AS plus AT$_{eff}$ model (dash-dotted curves). The SC-HRT outputs based on the AS pair potential only (dotted curves) and part of the $S(k)$ data of Refs. [3] (open circles) are also shown when available. Solid squares are the thermodynamic [16] $S(0)$ values. (a) $T = 169$ K. Neutron data and theoretical results for the 14.23 nm^{-3} state have been shifted upwards by 0.1. (b) $T = 199$ K. Data and theoretical curves for the 11.66 nm^{-3} and 11.31 nm^{-3} states have been shifted upwards by 0.5 and 1.3, respectively.

We have computed $S(k)$ also with the MHNC equation extended to include the effects of three-body forces [13]. This is known to be one of the most accurate theories of the short-range structure of simple fluids over a wide range of temperature and density, and in fact it gave results in excellent agreement with the previous measurements in the dense regime and at large k [3]. Conversely not too much is known about the accuracy of the MHNC theory on the small-k region, and it is known that the MHNC equation completely

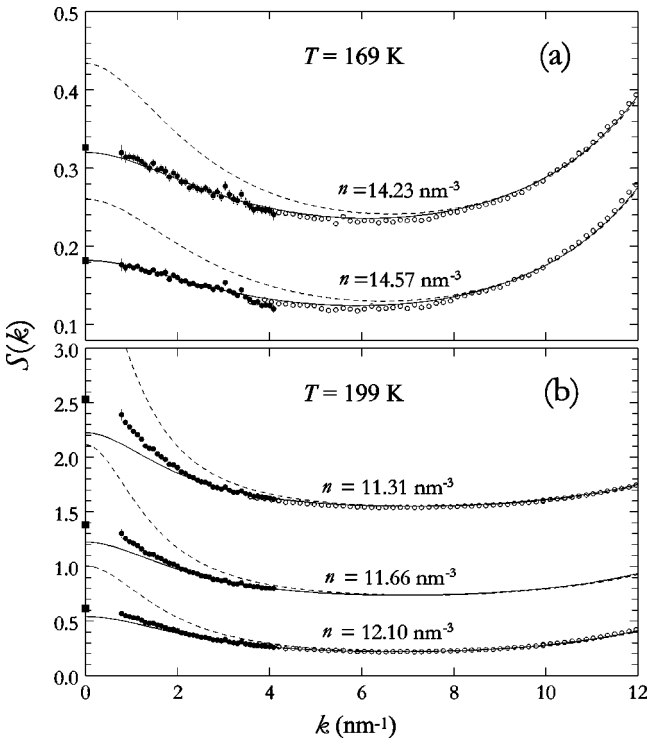

FIG. 2. As in Fig. 1, with the difference that data are compared with MHNC results for the AS (dashed curves) and for the AS plus AT (solid curves) interaction. (a) $T=169$ K. (b) $T=199$ K.

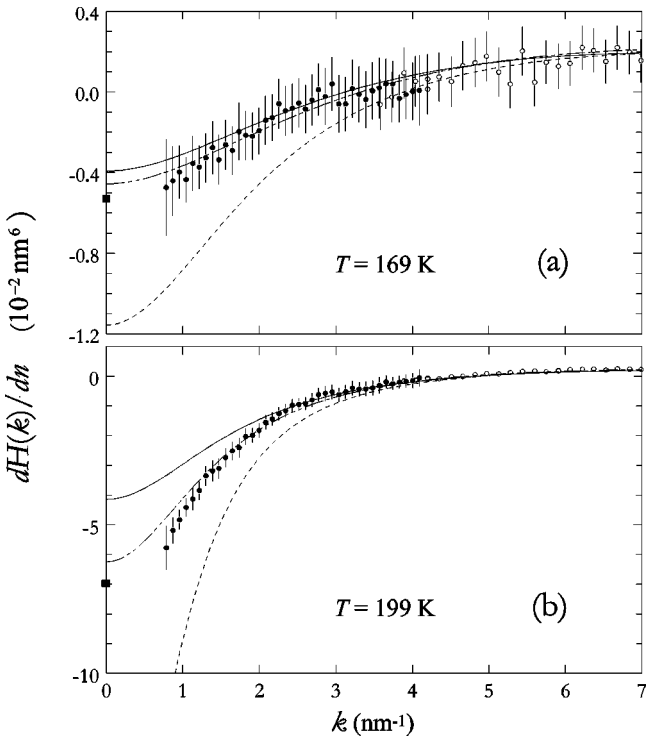

FIG. 3. Experimental density derivative of $H(k)$ in the low-k region (dots with error bars). Data at higher k values (open circles) are from Refs. [3]. The SC-HRT prediction based on the AS plus AT_{eff} interaction (dash-dotted curve) is shown, together with the MHNC results based on the AS (dashed curve) and on the AS plus AT (solid curve) potential. Solid squares at $k=0$ are the thermodynamic limits [16]. (a) $dH(k)/dn$ at $T=169$ K and $n=14.40$ nm^{-3}. (b) $dH(k)/dn$ at $T=199$ K and $n=11.66$ nm^{-3}. The derivative from the data of Refs. [3] is at the slightly different density $n=11.57$ nm^{-3}.

fails close to the critical point, where the reduced isothermal compressibility $S(k=0)$ is large compared to unity. In fact, under such conditions, the MHNC equation has no physical solution, and thus no true critical point, with diverging $S(0)$ and correlation length. In the absence of a critical point with the MHNC approach, we have no reason to modify the standard value of ν of the three-body AT interaction. We will comment below on the effect of using ν_{eff}.

In Fig. 2 the neutron data are compared with the MHNC results obtained by using the AS pair potential, with and without the AT interaction. Differences between the experimental $S(k)$ and the two-body results are again evident at low k: they increase with decreasing density and vary, at the lowest k, from 40% at 169 K to 70% at 199 K. The inclusion of long-range triple-dipole AT interactions provides a very good agreement at 169 K, and reduces the MHNC deviation from the 199 K data by nearly one-third. Residual deviations are seen to increase with approaching the coexistence region at 199 K, and also a slight (3%) deviation is detectable at 169 K for the 14.23 nm^{-3} state, which is closer to this boundary.

TABLE I. $S(0)$ values of liquid Kr at three different temperatures, as obtained from thermodynamic data [16] and from MHNC calculations using the AS plus AT and the AS plus AT_{eff} interaction.

T (K)	n (nm^{-3})	$S(0)^{expt}$ [16]	$S(0)_{\nu}^{MHNC}$	$S(0)_{\nu_{eff}}^{MHNC}$
199	11.66	0.880	0.7144	0.5251
169	14.57	0.182	0.1834	0.1532
130	16.83	0.064	0.071	0.063

We note that the use of the renormalized AT amplitude $\nu_{eff}>\nu$ in the MHNC calculations would lead to an even larger underestimation of the experimental $S(k)$ at 199 K and to a worse agreement at 169 K, as suggested also by the results of Fig. 2. This conclusion is further supported by the $S(0)$ data shown in Table I for two states on the 199 K and 169 K isotherms, respectively.

Differently, at higher liquid densities of Kr, such as those investigated at large k on the 130 K isotherm [3], the MHNC result with ν_{eff} provides an $S(0)$ value which is closer to the experimental one, as also reported in Table I. Therefore, for the densest fluid states near to the triple point, where the MHNC equation is expected to be particularly accurate, the AS plus AT_{eff} model is again a suitable effective interaction, able to explain the experimental results also by the MHNC theory. On the other hand, for states closer to the critical region or the coexistence boundary, the departures from experiment of MHNC (using ν_{eff}) might be evidence of the reduced accuracy of the integral equation in reproducing the long-wavelength space correlations.

As with the previous wide-angle data of Refs. [3], the studied thermodynamic states allow an experimental determination of the density derivative of $S(k)$ along both investigated isotherms. The thermodynamic derivatives of $S(k)$ of

simple liquids have been shown [3,18] to be very effective, more than $S(k)$ itself, for probing the microscopic interaction. In addition, more reliable conclusions can generally be drawn by analyzing the derivatives, since most of the possible systematic errors in the measurements and in the calculations are removed in a differential quantity. This is confirmed by the results of Fig. 3, where the experimental density derivative of $H(k)=[S(k)-1]/n$, at 169 and 199 K, is compared with the SC-HRT result based on the AS plus AT_{eff} model and with the MHNC prediction both for the AS and for the AS plus AT interaction. In fact, SC-HRT provides the best description of the low-k data even at 169 K [Fig. 3(a)], so that the small deviations of SC-HRT from the $S(k)$ data [see Fig. 1(a)] are found to be totally removed, at least in the experimental low-k range, when $dH(k)/dn$ is analyzed.

The convenience of referring to the derivatives when probing the interatomic interactions is also clear: the deviation in $dH(k)/dn$ of the MHNC two-body calculation from the neutron data at 169 K is of the order of 100%, i.e., more than twice the corresponding variation in $S(k)$ itself [$\sim$40%, Fig. 2(a)]. By adding the triplet AT contributions, the experimental behavior of the 169 K derivative is rather closely reproduced by the MHNC result, though less satisfactorily than with SC-HRT. On the other hand, deviations (reaching 42%) of the triplet MHNC calculations from the $dH(k)/dn$ data are present at 199 K for $k<2.5$ nm^{-1}, while SC-HRT is able to account very well for the experimental derivative down to $k\sim1.2$ nm^{-1}.

In conclusion, the present study proves that three-body forces have a major role in determining the structure of a simple liquid as Kr for k values smaller than the position of the first minimum of $S(k)$, and provides convincing evidence for the presence of additional many-body contributions beyond the long-range triple-dipole AT interaction. Both the thermodynamic properties and the low-k behavior of structural quantities are quite remarkably accounted for by SC-HRT using, as effective many-body potential, an AT interaction of renormalized (65% higher) intensity. By comparing diffraction data with two-body calculations, the size of many-body effects on the low-k structure of liquid Kr ($1.7<n/n_c<2.2$) has been evaluated to amount to more than 40% for $S(k)$ and even 100% for $dH(k)/dn$.

The overall nice agreement of SC-HRT with experiment, at all the investigated liquid densities, is confirmed, in particular, by the low-k behavior of $dH(k)/dn$. A less accurate description of the diffraction data at small k values is achieved with MHNC calculations, especially in the vicinity of the critical or coexistence regions. This is probably due to the difficulties of the MHNC approach in properly accounting for increasing long-wavelength density fluctuations, rather than indicating some significant inadequacy in the assumed AS plus AT_{eff} realistic model. We showed, in fact, that where the MHNC theory is highly accurate, the above effective interaction provides the best agreement with the experimental compressibility of Kr.

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