Neutron Diffraction Study of Liquid Krypton and the Interatomic Interaction

F. Barocchi,[1] P. Chieux,[2] R. Magli,[3] L. Reatto,[4] and M. Tau[5]
[1] *Dipartimento di Fisica, Università degli Studi, largo Fermi 2, I50125 Firenze, Italy*
[2] *Institut Laue-Langevin, 156X, 38042 Grenoble CEDEX, France*
[3] *Dipartimento di Energetica, Università degli Studi, via di S. Marta 3, I50139 Firenze, Italy*
[4] *Dipartimento di Fisica dell' Università, via Celoria 16, I20133 Milano, Italy*
[5] *Dipartimento di Fisica dell' Università, viale delle Scienze, I43100 Parma, Italy*
(Received 26 October 1992)

We show that diffraction measurements can reach the precision needed to test different models of interatomic interaction also in a dense fluid. Our measurements have been performed in krypton at several temperatures and densities in the liquid phase. Our theoretical calculations show that the density derivative of the static structure, contrary to the function itself, is sensitive to the shape of the interaction and the comparison with the experimental data gives another test of the interaction models.

PACS numbers: 61.25.Bi, 61.20.Gy

One of the motivations for the accurate determination of the static structure of a fluid is that the radial distribution function $g(r)$ and the related static structure factor $S(k)$ contain detailed information on the interatomic interaction. Recently [1] it has been shown that $S(k)$ can be determined now by neutron scattering with the accuracy necessary to obtain an unambiguous determination of the pair interatomic interaction $u_2(r)$ in low density fluid argon. In that case $S(k)$ directly reflects u_2. The situation is quite different in a dense fluid where the structure is dominated by excluded-volume effects, i.e., by the strong repulsive forces which are present at short interatomic distances. In fact it is well known that $S(k)$ of such diverse fluids like liquid argon or molten sodium can be modeled very simply by the structure factor of hard spheres. What is an asset in the theory of liquids [2], i.e., the weak dependence of $S(k)$ on the detailed shape of the interatomic forces, makes it very difficult to extract information on these forces from the measured $S(k)$. This is particularly true in rare gases in which the repulsive forces are very harsh and it was not clear that different models of interatomic interaction could be really tested by a measurement of $S(k)$ in the dense phase. The case of krypton is particularly significant because the rather large deviation between the measured [3] $S(k)$ and the computed one [4] with the best models [5, 6] of the interatomic interaction raised questions on the accuracy of these models of interaction and on the role of many-body forces.

With this in view we have performed a new set of measurements of $S(k)$ in liquid Kr at several densities and temperatures and over an extended k range. We find that the higher accuracy with which now $S(k)$ can be determined allows for an unambiguous test of different models of interatomic interaction. By using an accurate theory of liquid structure, the modified hypernetted chain (MHNC) equation [7] extended, when needed, to include three-body forces [8], we show that the hard sphere and the Lennard-Jones (LJ) potentials give an inadequate representation of the forces whereas the Barker [5] and the Aziz HFD-B models [6] of $u_2(r)$ are very satisfactory. Our diffraction data taken together with thermodynamic data indicate also that many-body forces must be present and the Axilrod-Teller-Muto (ATM) [9] triple dipole $u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ gives a first good account for these forces for the description of the static properties of this liquid. In addition, from our theoretical study we find that the derivative of structural data with respect to the density n can be very sensitive to the shape of the interatomic potential. If we write

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

so that $H(k)$ contains all the structural information because $H(k)$ is given by

$$H(k) = \int d^3r[g(r) - 1]e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2}$$

we find that $\partial H(k)/\partial n$ can change by as much as 50% when $u_2(r)$ is changed from the Aziz u_2, for instance, to the LJ one. Our measurements give access also to this derivative $\partial H(k)/\partial n$ and also on this basis we are able to test the models of interaction.

The neutron diffraction measurements were performed at the Institut Laue-Langevin in Grenoble by means of the D4B diffractometer. The scattered intensities were measured with two ^{3}He multidetectors over the range $3.6 < k < 162.4$ nm^{-1}. Details of the experiment and the corrections of the data due to background, multiple scattering, attenuation effects, and effects for the inelastic scattering are described elsewhere [10]. In order to obtain $S(k)$ from the scattered intensities one needs the absolute normalization of the data and the ratio σ_S/σ_c between total and coherent scattering cross section. As a result of the extended k range of our measurement the normalization is obtained by the condition that $S(k)$ converges to 1 at large k. The ratio σ_S/σ_c is not well known

and deviations as large as 10% have been reported. In this situation we have adopted for σ_S/σ_c the value which brings one of our $S(k)$ in the small-k region to agree with the $k = 0$ compressibility limit $S(0) = n k_B T \chi_T$. This has been performed for the measurement at $T = 169$ K and $n = 14.57$ nm^{-3} because for this state the theoretical result for the isothermal compressibility χ_T is very close to experiment so that one can use with confidence the theoretical $S(k)$ behavior in order to normalize the data at low k to the experimental $S(0)$ value given by the compressibility limit. This procedure leads to the value $\sigma_S/\sigma_c = 1.068$.

The MHNC is an integral equation for $g(r)$ given a pair interaction $u_2(r)$. The approximation inherent to this equation is the replacement [7] of the unknown bridge function $E(r)$ relative to u_2 by the same function appropriate to hard spheres of a suitable diameter. The MHNC equation has been extended [8] to take into account the presence of a three-body interaction u_3 by including the term of $E(r)$ which is of lowest order in u_3. The accuracy of MHNC is well documented [2, 11, 12] for quite different forms of u_2. Comparison with simulation results indicates that the typical level of inaccuracy of $g(r)$ given by MHNC is below 0.05 in the region of the triple point and a substantially lower level of inaccuracy is present at smaller density. The effect on $g(r)$ of u_3 of the ATM form is given very accurately by the triplet MHNC [4].

For krypton two models for u_2 have been widely used. The first has been introduced by Barker *et al.* [5] and the second is the HFD-B model derived later by Aziz *et al.* [6]. The Aziz u_2 has the advantage that it is independent of solid-state data but the two potentials turn out to be very similar. For u_3 we have used the ATM form with intensity $\nu = 220.4 \times 10^{-84}$ erg cm^9. In addition we have considered the LJ form with parameters [2] $\epsilon_{\rm LJ}/k_B = 166.2$ K and $\sigma_{\rm LJ} = 0.368$ nm (these give the best representation of the second virial coefficient) and also for other choices. Finally we have considered the hard sphere potential and in this case we have used the Verlet-Weis parametrization [2] of $g(r)$ and $S(k)$.

The measurements have been performed at three temperatures, $T = 199$ K, $T = 169$ K, and $T = 130$ K and at densities $n = 11.86$ and 11.28 nm^{-3} at the higher T, $n = 14.57$, 14.40, and 14.25 nm^{-3} at $T = 169$ K, and $n = 17.01$ and 16.83 nm^{-3} at the lower T. Thus we explore the T range from almost the triple point to about 5% below the critical temperature and the density is slightly higher than that of the liquid at coexistence. As an example in Fig. 1 we show $S(k)$ at $T = 169$ K and $n = 14.57$ nm^{-3}. On the scale of the figure the measured $S(k)$ is indistinguishable from the theoretical result. This refers to the Aziz model of u_2 plus the ATM u_3. Similar agreement between theory and experiment is found for all the other states of our measurements [13]. The effect on $S(k)$ of changing the interaction is rather small so that in Fig. 1 we give also the deviation plot; i.e., we plot $\Delta S(k) = S_{\rm exp}(k) - S_{\rm MHNC}(k)$ vs k for the Aziz u_2

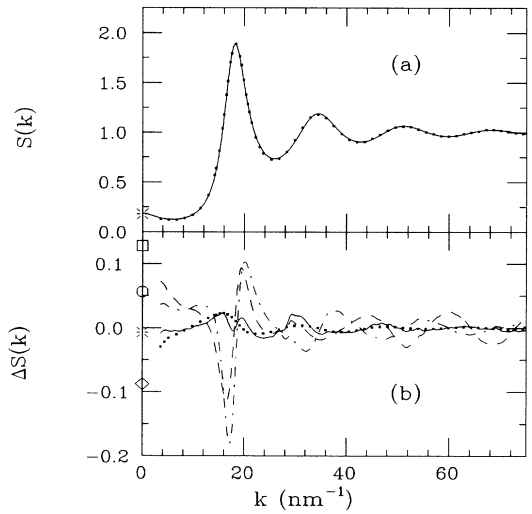

FIG. 1. (a) Theoretical (full curve) and experimental (•) $S(k)$ at $T = 169$ K, $n = 14.57$ nm^{-3}. Value at $k = 0$ from the compressibility data [18] (∗). (b) Difference $\Delta S(k) = S_{\rm exp}(k) - S_{\rm MHNC}(k)$ for the Aziz pair interaction with (full curve) and without the ATM three-body term (dotted curve), for the LJ interaction (dot-dashed curve), and for hard spheres (dashed curve). Symbols (∗, ◇, ○, □) at $k = 0$ are for the different interactions in the order as above.

with and without u_3, for the LJ potential, and for hard spheres of diameter such that the height of the main maximum of $S_{\rm HS}(k)$ matches the experimental value. For the Aziz u_2 $|\Delta S(k)|$ is everywhere below 0.03 and for $k \gtrsim 40$ nm^{-1} $\Delta S(k)$ is within the noise level of experiment. The deviation plot for the Barker u_2 is not shown because it is almost indistinguishable from that for the Aziz u_2. In fact in the r range which is relevant here these two model interactions are very close, for instance the difference in the depth well is just 1% . On the other hand, $\Delta S(k)$ for the LJ u_2 and for hard spheres is substantially larger at all k and the deviation is particularly large in the region of the main maximum of $S(k)$. We have considered also other suggested choices of the parameters $\epsilon_{\rm LJ}$ and $\sigma_{\rm LJ}$ but we do not find significant changes in $\Delta S(k)$ so that the inaccurate representation of $S(k)$ is intrinsic to the LJ potential.

It is important to perform the comparison also in r space in terms of $g(r)$. In order to obtain $g(r)$ from $S(k)$ via the inverse Fourier transform of Eqs. (1), (2) it is necessary to extend the measured $S(k)$ at small and at large k. Because of the extended k range of the measurement and the excellent agreement between theory and experiment, we have used a rather simple procedure: at large k we have simply switched from the measured $S(k)$ to the theoretical value for one of the interaction models which gives a good representation of $S(k)$, i.e., the Aziz u_2 plus the ATM u_3. At small k, $S(k)$ is extended by means of the theoretical MHNC behavior; an extension with a

fourth-order polynomial in k to the thermodynamic value of $S(0)$ has been also applied and does not change the resulting $g(r)$. $g(r)$ corresponding to the data of Fig. 1 is compared to theory in Fig. 2. The small amplitude of the oscillations around zero of $g(r)$ at short distance indicates the accuracy of the data and of the extension method. Also for $g(r)$, the result for the Aziz u_2 plus the ATM u_3 is almost indistinguishable from experiment. In terms of the deviation plot for $\Delta g(r) = g_{\rm exp}(r) - g_{\rm MHNC}(r)$ it is again clear that the LJ interaction does not give an accurate representation of correlation in dense krypton and that the Aziz u_2 is quite satisfactory. The ATM three-body u_3 gives a better representation of $g(r)$ in particular at short distance. This taken together with the necessity [14] of introducing u_3 in order to get a good representation of the equation of state when an accurate u_2 is used gives a strong indication that the ATM u_3 is a substantially correct representation of three-body forces. The accuracy of our data is not enough to distinguish between the Barker and the Aziz u_2. The comparison between theory and experiment for the other states of our experiment agrees completely with that which is discussed here. The small remaining deviations between experiment and theory for the best model interaction increase with density and give indication [13] for small additional forces of many-body character which are repulsive at short distance and attractive at larger distance. However, a detailed analysis of these additional forces requires a careful study of the effects of the approximation built in MHNC and of the extension of the measured $S(k)$ at small and at large k.

The measurement of $S(k)$ at closely spaced densities gives access to the isothermal density derivative $\partial H(k)/\partial n$. Notice that the changes in density are of order 1% at the two lower T and 6% at the higher T. The results at the three temperatures of our measurement are shown in Fig. 3. Here we show also the MHNC result for the different models of interaction. Also for theory $\partial H(k)/\partial n$ represents the finite difference ratio computed with the same densities of experiment. In a derivative quantity obtained from two independent measurements the effect of noise is much larger but the accuracy of our measurement permits a good determination of $\partial H(k)/\partial n$ up to $k \simeq 25$ nm^{-1}. On the theoretical side one notices the large difference between $\partial H(k)/\partial n$ for the Aziz and for the LJ u_2. The typical change of $S(k)$ for these two pair interactions is in the range of 0.1, i.e., of order of 5% of $S(k)$ in the region of the maximum. A difference 10 times larger is found when we consider $\partial H(k)/\partial n$. The different shape of u_2 for the two models of interaction has the consequence that the position and the height of $S(k)$ change with density more strongly for the LJ than for the Barker or the Aziz u_2. Also in terms of $\partial H(k)/\partial n$ the experimental data are in good agreement with the result for the accurate form of u_2 and strongly disagree with the

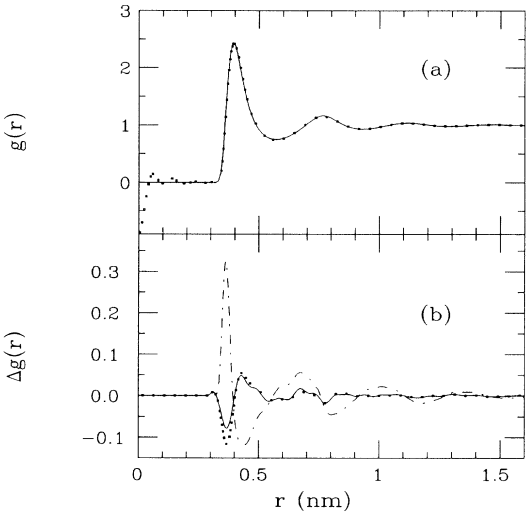

FIG. 2. (a) Theoretical (full curve) and experimental (•) $g(r)$ at $T = 169$ K, $n = 14.57$ nm^{-3}. (b) Difference $\Delta g(r) = g_{\rm exp}(r) - g_{\rm MHNC}(r)$ for the Aziz pair interaction with (full curve) and without (dotted curve) the ATM three-body interaction and for the LJ interaction (dot-dashed curve).

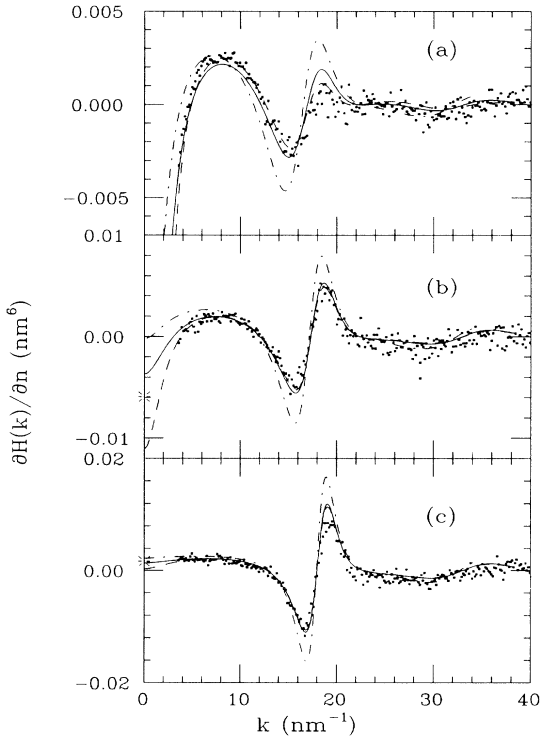

FIG. 3. $\partial H(k)/\partial n$ for the Aziz pair interaction with (full curve) and without the ATM three-body term (dashed curve), for the LJ interaction (dot-dashed curve), and from experimental data (•) at (a) $T = 199$ K, (b) $T = 169$ K, (c) $T = 130$ K. Value at $k = 0$ from the compressibility data [19] (*).

LJ result. The effect of u_3 on $\partial H(k)/\partial n$ is rather small at medium and large k but it becomes very significant for $k \lesssim 3$ nm^{-1}. In this respect it would be important to extend the measurement down to $k \sim 1$ nm^{-1}. We notice that this is also the range which should allow [15] one to get better evidence and comparison between theory and experiment for the nonanalytic $|k|^3$ term in $S(k)$ due to the long-range dispersion forces [16, 17].

In conclusion, we have shown that it is now possible to measure $S(k)$ with the accuracy which is needed to get information on the detailed shape of the interatomic interaction even in the region of the triple point. The dependence of $S(k)$ and $g(r)$ on the shape of the pair interaction u_2 is small but we have shown that a determination of $S(k)$ with a precision of a few parts per thousand gives rich information. We find that the LJ model is an inadequate representation of the forces but the Barker or the Aziz u_2 is satisfactory. The agreement between theory and experiment is quite remarkable for all the states of our measurements. We start to get evidence also from structural data that the three-body ATM u_3 improves the description of the system and this agrees nicely with the result for thermodynamic properties [14].

The density derivative of the pair correlation function is important because it contains information on three-body correlations [18]. We find that the quantity $\partial H(k)/\partial n$ is important also because it is much more sensitive to the interaction than $H(k)$ itself. This is mainly due to the fact that the density variation of the height, position, and width of the main peak of $S(k)$ is rather different for the various potentials and a difference of more than 50% is found between $\partial H(k)/\partial n$ for the LJ and that for the accurate u_2. Also in this respect our experimental result indicates quite clearly the superiority of the Barker and the Aziz u_2 over the LJ form. Extension of the measurement to smaller k should be able to provide evidence for the presence of the ATM u_3.

The scattering cross sections of Kr are not known with enough precision and we have overcome this by using the condition that $S(k)$ at small k should extrapolate to the thermodynamic value of $S(0)$. This is a sensible procedure but an independent determination of high accuracy of these cross sections is important.

This work was partially supported by Consorzio INFM and by MURST.

[1] H. Fredrikze, J. B. van Tricht, A. A. van Well, R. Magli, P. Chieux, and F. Barocchi, Phys. Rev. Lett. **62**, 2612 (1989).
[2] J. P. Hansen and I. R. Mc Donald, *Theory of Simple Liquids* (Academic, London, 1986).
[3] A. Teitsma and P. A. Egelstaff, Phys. Rev. A **21**, 367 (1980).
[4] M. Tau, L. Reatto, R. Magli, P. A. Egelstaff, and F. Barocchi, J. Phys. Condens. Matter **1**, 7131 (1989).
[5] J. A. Barker, R. O. Watts, J. K. Lee, T. P. Shafer, and Y. T. Lee, J. Chem. Phys. **61**, 308 (1974).
[6] R. Aziz and M. J. Slaman, Mol. Phys. **58**, 679 (1986).
[7] Y. Rosenfeld and N. H. Ashcroft, Phys. Rev. A **20**, 1208 (1979).
[8] L. Reatto and M. Tau, J. Chem. Phys. **86**, 6474 (1987).
[9] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943); Y. Muto, Proc. Phys. Math. Soc. Jpn. **17**, 629 (1943).
[10] F. Barocchi, P. Chieux, and R. Magli (to be published).
[11] F. Lado, S. M. Foiles, and N. W. Ashcroft, Phys. Rev. A **28**, 2374 (1983).
[12] L. Reatto, D. Levesque, and J. J. Weis, Phys. Rev. A **33**, 3451 (1986).
[13] F. Barocchi, P. Chieux, R. Magli, L. Reatto, and M. Tau (to be published).
[14] J. A. Barker, Phys. Rev. Lett. **57**, 230 (1986).
[15] L. Reatto and M. Tau, J. Phys. Condens. Matter **4**, 1 (1992).
[16] J. E. Enderby, T. Gaskell, and N. H. March, Proc. Phys. Soc. **85**, 217 (1965).
[17] F. Barocchi, P. Chieux, H. Fredrikze, and R. Magli, Physica (Amsterdam) **180** & **181B**, 877 (1992).
[18] F. P. Buff and R. Brout, J. Chem. Phys. **33**, 1417 (1960); P. Schofield, Proc. Phys. Soc. **88**, 149 (1966).
[19] W. B. Street and L. A. K. Staveley, J. Chem. Phys. **55**, 2495 (1971).